



THE ISOTOPE EFFECT IN VIBRATIONAL  
SPECTRA OF SIMPLE POLYATOMIC  
MOLECULES

BY

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THE ISOTOPE EFFECT IN VIBRATIONAL SPECTRA  
OF SIMPLE POLYATOMIC MOLECULES

by

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L. E. S.





## INTRODUCTION

An important source of information concerning the structure of matter is the analysis of the spectra of atoms and molecules in their different states of aggregation. In this thesis we are interested in the spectroscopic behaviour of molecules in their vapor state. Three different motions in molecules lead to the production of a spectrum, namely: electronic motion, vibration of the parts of the molecule against each other and rotation of the molecule as a whole. While the pure rotational spectrum can be observed alone, the vibrational spectrum is always superposed by a rotational one, and the electronic spectrum is always accompanied by a vibrational and a rotational spectrum. In a certain approximation the total energy of a molecule is represented by the sum of the electronic, vibrational and rotational energies. In this paper we will deal only with the infrared and Raman vibrational spectrum of some simple polyatomic molecules. Moreover, we will neglect the fine structure in these spectra resulting from rotational motion.

The production of a vibrational infrared spectrum is associated with a changing dipole moment in the molecule. This means that a vibrational motion gives rise to an infrared spectrum as



long as this motion causes a change in the dipole moment of the molecule. In the case of the Raman spectrum, the vibrations give rise to the spectrum because of the change in the polarizability associated with the motion.

Vibrations that do not appear in the infrared are called infrared inactive and those that appear in the infrared are called infrared active. A similar classification leads to a distinction of vibrations as being Raman active or Raman inactive. While some vibrations appear in both spectra others are only active in the Raman spectrum and inactive in the infrared, and vice versa.

The study of the vibrational spectrum of molecules is helpful in determining the geometrical shapes of molecules, bond angles, force constants, internuclear distances, vibrational levels, vibrational frequencies. However, there are very few cases in which a complete knowledge of the structure of a molecule has been obtained. Sometimes additional information may be had from the study of the isotope effect. This effect consists in a shift of the bands in the spectrum when some of the atoms in the molecule are substituted by isotopes. Some weak bands, previously unexplained in different spectra, have been found to be due to the presence of isotopic molecules. The isotope effect occurs also in electronic and pure rotational spectra. For example, the isotopes of oxygen, carbon and nitrogen were first discovered from the electronic spectra of the corresponding molecules.

Mathematical expressions based on different assumptions about the field of force in a molecule, have been derived for the calculation of the vibrational frequencies and also for the





frequency shifts upon isotopic substitutions.

In this thesis a brief discussion of vibrational motion in polyatomic molecules will be given with special reference to simple triatomic molecules. A general relation will be described concerning the isotope effect. In particular this relation will be applied to linear and non-linear symmetrical triatomic molecules. An empirical rule given in the literature will be discussed in connection with the general relation concerning the isotope effect.





## Chapter 1

### GENERAL THEORY

#### 1. The Harmonic Oscillator

Vibrations in molecules may be treated in first approximation as harmonic vibrations, as we will describe presently. The simplest example of harmonic motion is that of the so-called simple harmonic oscillator.

The equation of motion of a particle executing simple harmonic motion is

$$m \frac{d^2x}{dt^2} = - kx \quad (I, 1)$$

where  $k$  is the force constant and  $m$  is the mass of the particle. The solution of this differential equation may be written in the form

$$x = C \cos (\omega t + \delta ). \quad (I, 2)$$

Here  $\omega = \sqrt{\frac{k}{m}}$ , and  $C$  and  $\delta$  are constants of integration. Since the cosine function is periodic of period  $2\pi$  and varies from  $+1$  to  $-1$  through  $0$ , the motion is seen to be vibrational about the equilibrium position  $x = 0$ , and has a maximum displacement or



amplitude  $C$ . The argument of the cosine is called the phase angle or the phase.  $\delta$  is the phase at  $t = 0$  and is sometimes called the epoch angle. The constant  $\omega$  determines the period of the vibration, i.e., the time required by the particle at any position to return to the same position going in the same direction.

If we call  $T = \text{period}$

$$\omega(t + T) + \delta = \omega t + \delta + 2\pi$$

$$2\pi = \omega T$$

$$T = 2\pi \sqrt{\frac{m}{k}}.$$

Since the frequency  $\nu = 1/T$ , then

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{m}}. \quad (\text{I, } 3)$$

This equation states that the frequency of a harmonic oscillator depends only on the mass of the particle and on the force constant  $k$ , and not on the amplitude of the vibration.

The potential energy of the harmonic oscillator at any position  $x$ , with respect to the position  $x = 0$  is

$$V = - \int_0^x -k x \, dx = \frac{1}{2} kx^2. \quad (\text{I, } 4)$$

This means that in a harmonic oscillator the potential energy depends on the square of the displacement from the equilibrium position.

In a diatomic molecule, instead of only one particle, we





have two particles vibrating against each other. If we assume in first approximation, that the restoring forces on both atoms are proportional to the displacements from the equilibrium position, the motion of both particles is considered simple harmonic. This system of two coupled masses may be reduced to the model of

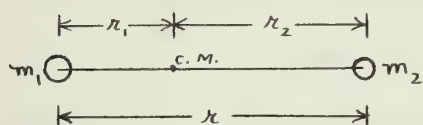


Fig. 1

a simple harmonic oscillator in the following way. Let  $m_1$  and  $m_2$  be the masses of the two atoms. If  $r_1$  and  $r_2$  are the distances of  $m_1$  and  $m_2$  from the center of mass of the molecule, then the equations of motion of both particles are

$$m_1 \frac{d^2 r_1}{dt^2} = -k(r - r_e) \quad (\text{I, 5})$$

$$m_2 \frac{d^2 r_2}{dt^2} = -k(r - r_e) \quad (\text{I, 6})$$

where  $r$  is the instantaneous separation of both atoms and  $r_e$  is their separation at their equilibrium position. Also

$$r_1 = \frac{m_2}{m_1 + m_2} r \quad \text{and} \quad r_2 = \frac{m_1}{m_1 + m_2} r. \quad (\text{I, 7})$$

On substituting these expressions in (I, 5) and (I, 6), we obtain by combining both equations

$$\frac{m_1 m_2}{m_1 + m_2} \frac{d^2(r - r_e)}{dt^2} = -k(r - r_e). \quad (\text{I, 8})$$



This is the equation of a harmonic oscillator of mass  $\mu = \frac{m_1 m_2}{m_1 + m_2}$ .  $\mu$  is called the reduced mass. The frequency of vibration is

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}. \quad (1, 9)$$

In the case of polyatomic molecules the situation is not so simple since the different atoms are involved in different vibrations. In general, a molecule performs a motion which is a combination of translation, rotation and vibration. The total number of degrees of freedom of a molecule of  $N$  atoms is  $3N$ , of which, three correspond to translation of the center of mass along the three coordinate axes, and three correspond to rotation about the three axes if the molecule is non-linear. If the molecule is linear it has only two rotational degrees of freedom, since rotation about the internuclear axis does not change the position of the nuclei. Therefore, a molecule has  $3N - 6$  or  $3N - 5$  vibrational degrees of freedom according to whether it is linear or non-linear, respectively. It can be shown that the number of vibrational degrees of freedom gives the number of different vibrations. In each of these vibrations the atoms describe, in first approximation, a simple harmonic motion. Any complicated vibrational motion of a molecule can namely be resolved into simple harmonic motions. These simple vibrations are called normal vibrations or normal modes of vibration, and their total number is  $3N - 6$  (or  $3N - 5$ ). Hence, a complicated vibrational motion in a polyatomic molecule may be reduced to that of a number of harmonic oscillators, in a manner similar to that by which a





diatomic molecule was reduced to one harmonic oscillator. We may include translations and rotations as oscillations of frequency 0, in which case they are called non-genuine vibrations. The real vibrations are called genuine vibrations. The general motion of a molecule can then be represented as a superposition of  $3N$  normal vibrations, in which we include genuine and non-genuine vibrations.

## 2. The Secular Equation<sup>1</sup>

Let us consider a molecule, in space, of  $N$  atoms which are in their equilibrium positions. As long as these particles remain in their equilibrium positions, the molecule may be considered as a rigid body. Suppose now that one atom  $j$  is displaced giving rise to restoring forces on the rest of the atoms and on itself. These forces depend on the displacement of the  $j$ -th atom from its equilibrium position. Therefore the components of the forces on the atoms, along the  $x, y, z$  coordinates fixed in space, depend on the  $x_j, y_j, z_j$  components of the displacement of atom  $j$ . Let us consider atom 1 and the components  $F_x^1, F_y^1, F_z^1$  of the force on it due to the displacements of all atoms  $j$ .

$$F_x^1 = F_x^1(x_1, y_1, z_1, x_2, y_2, z_2, \dots, x_j, y_j, z_j, \dots, z_N),$$

$$F_y^1 = F_y^1(x_1, y_1, z_1, x_2, y_2, z_2, \dots, x_j, y_j, z_j, \dots, z_N), \quad (I, 10)$$

$$F_z^1 = F_z^1(x_1, y_1, z_1, x_2, y_2, z_2, \dots, x_j, y_j, z_j, \dots, z_N).$$

These expressions merely state the dependence of the forces on the displacements from the equilibrium positions. We can write down similar expressions for atoms 1, 2, 3, ...,  $N$ . Assuming



that the functions (I, 10) can be expanded in power series, and that the displacements are small, we can neglect terms of higher order than the first and we obtain for the x component of the force on any particle i:

$$F_x^i = k_{xx}^{i1}x_1 + k_{xy}^{i1}y_1 + k_{xz}^{i1}z_1 + k_{xx}^{i2}x_2 + \dots + k_{xz}^{iN}z_N.$$

Writing similar expressions for the y and z components  $F_y^i$  and  $F_z^i$ , leads to the following system of equations for all atoms i.

$$\begin{aligned} F_x^i &= k_{xx}^{i1}x_1 + k_{xy}^{i1}y_1 + k_{xz}^{i1}z_1 + k_{xx}^{i2}x_2 + \dots + k_{xz}^{iN}z_N, \\ F_y^i &= k_{yx}^{i1}x_1 + k_{yy}^{i1}y_1 + k_{yz}^{i1}z_1 + k_{yx}^{i2}x_2 + \dots + k_{yz}^{iN}z_N, \quad (\text{I, 11}) \\ F_z^i &= k_{zx}^{i1}x_1 + k_{zy}^{i1}y_1 + k_{zz}^{i1}z_1 + k_{zx}^{i2}x_2 + \dots + k_{zz}^{iN}z_N. \end{aligned}$$

Since i takes values  $i = 1, 2, 3, \dots, N$  (for a polyatomic molecule of N atoms), this is a system of  $3N$  equations in the  $3N$  unknowns  $x_1, y_1, z_1, x_2, \dots, z_N$ .

The constants k are force constants. They are negative because of the restoring nature of the forces.  $k_{xy}^{ij}$  tells how the x component of the force on the i-th particle depends on the y component of the displacement of the j-th particle. The relation  $k_{xy}^{ij} = k_{yx}^{ji}$  holds. It also holds for k's involving subscripts z.<sup>2</sup>

In order that the motion be simple harmonic the forces  $F_x^i, F_y^i, F_z^i$  for all i's must be of the form









Equation (I, 14) is called the secular equation. For a particular  $\nu$  given by the secular equation, the solution of (I, 13) gives the displacements of the atoms in the corresponding normal vibration.

The frequencies of the vibrations are observed in the spectrum. By substituting each of these observed frequencies in the secular equation we obtain a number of simultaneous equations in the unknown force constants. However, the force constants cannot be calculated from these relations because the number of unknowns is greater than the number of equations. Therefore, we have to introduce certain assumptions about the field of force in a molecule, in order to reduce the number of force constants, or else we have to look for additional information.

There are two important assumptions about the field of force in a molecule, that of the so-called central force field and that of the valence force field. In the central force field the force acting on a given atom is the resultant of the attractions and repulsions by all the other atoms, and these attractions and repulsions depend only on the distances from these other atoms and lie in lines connecting them with the one considered. In the valence force field there is a strong restoring force in the line of every valence bond when the distance of the two atoms bound by this bond is changed; in addition, there is a restoring force opposing a change in the angle between two valence bonds connecting one atom with two others. Equations have been derived, using the mentioned assumptions, from which force constants and bond angles may be calculated.





As has been said one way of obtaining more information for the calculation of the force constants and for the determination of the structure of a molecule, is by making use of the isotope effect. Since the nature of the electronic bond is not changed when isotopes are substituted, the force constants remain the same, but since the masses are slightly different the frequencies differ from those of the ordinary molecule. If one or more isotope molecules are known, their observed frequencies and corresponding isotopic masses may be substituted in the secular equation in order to obtain more relations necessary for the calculation of all force constants. Such a calculation may be achieved in general. Usually, assumptions regarding the field of force are introduced to facilitate the evaluation of force constants.

There are cases in which the isotopic shift does not depend on the force constants but only on the atomic masses and on the geometrical structure of the molecule. Moreover, it will be seen in a later chapter that the vibrations of a molecule can always be grouped according to their symmetry properties, and that the isotopic shifts of each particular group of frequencies obey a relation which is independent of the force constants. Before discussing this relation it is important to consider the model of the anharmonic oscillator and to give a brief discussion of symmetry properties of molecules and vibrations.

### 3. The anharmonic oscillator and its application to the vibrations



of polyatomic molecules.

a) Classical comparison of harmonic and anharmonic motions.

We have seen that a particle which moves along the x-axis and has a potential energy  $V$  proportional to the square of the

displacement from the equilibrium position ( $V = \frac{1}{2} kx^2$ ), is describing a simple harmonic motion and its frequency is independent of the amplitude of the vibration. The curve potential energy versus displacement is a parabola, see Fig. 2.

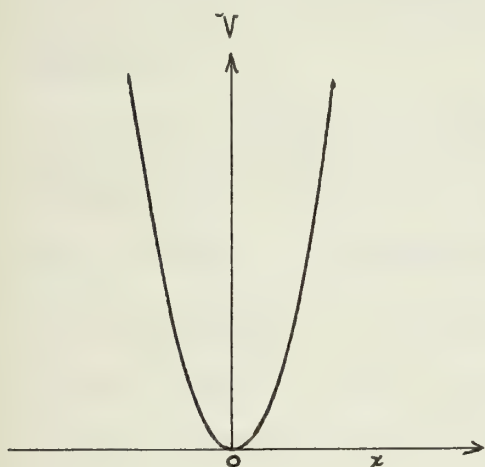


Fig. 2

It was mentioned before that in a diatomic molecule the vibration of the two atoms against each other can be

considered simple harmonic only in first approximation. Actually, when the two atoms are separated by a large distance, the attractive force is zero. Correspondingly, at this large separation,

the potential energy is a constant.

If the two atoms are brought very close to each other the repulsive force increases very fast. Then, the actual potential curve takes the form of Fig. 3. The curve is approximately a parabola only in the neighborhood of the minimum which corresponds to the equilibrium

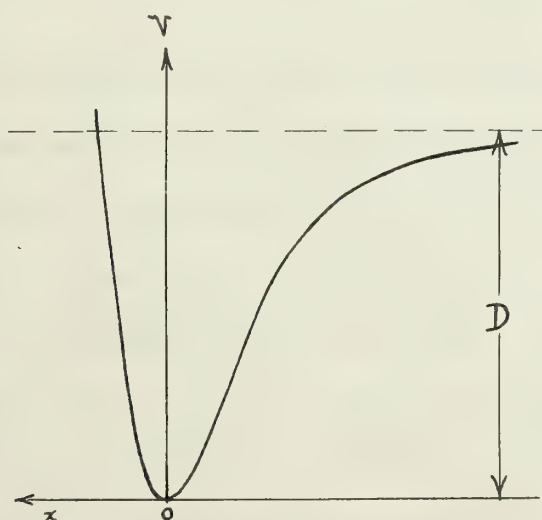


Fig. 3





position. The potential energy of the molecule can be represented by

$$V = kx^2 + k_1x^3 + k_2x^4 + \dots \quad (I, 15)$$

where  $x = -(r - r_e)$ , and the molecular motion is said to be anharmonic.

If a single particle on the  $x$ -axis moves under the action of a force such that its potential energy is of the form of (I, 15), this particle is called an anharmonic oscillator. Just as the harmonic motion of a two particle system was reduced to the model of one harmonic oscillator, the anharmonic motion of an actual diatomic molecule may be reduced to the model of one anharmonic oscillator.

The solution of the differential equation of motion for the anharmonic oscillator is not represented by a simple cosine or sine function but by a Fourier series

$$x = A_0 \cos \omega t + A_1 \cos 2\omega t + A_2 \cos 3\omega t + \dots \quad (I, 16)$$

This expression states that the motion can be considered as a superposition of simple harmonic vibrations whose frequencies are integral multiples of the first frequency  $\omega/2\pi$ . This is called the fundamental frequency and its integral multiples are called 1-st overtone, 2-nd overtone, 3-rd overtone, etc. For very small amplitudes ( $x \rightarrow 0$ ), terms of higher order than the first one can be neglected in (I, 15), and the anharmonic oscillator goes over into the harmonic oscillator. Thus, although the actual molecule is represented by the model of an anharmonic oscillator it is



permissible to describe its motion as that of a harmonic oscillator if vibrations are considered in the immediate neighborhood of the equilibrium position only. In this case the frequency of the oscillator is called the zero order frequency.

If more energy is given to the anharmonic oscillator than corresponds to the horizontal asymptote in Fig. 3, the particle is completely removed from the field of force and it does not come back to the equilibrium position. This corresponds, in the actual diatomic molecule to a complete separation of the two atoms. The energy necessary for this process is called the dissociation energy or heat of dissociation, and is denoted by  $D$  in Fig. 3.

In a polyatomic molecule the different vibrations are, more rigorously, also anharmonic vibrations rather than simple harmonic vibrations.

b) Quantum mechanical comparison of harmonic and anharmonic motions.

Let us consider Schroedinger's equation for a system of one particle of mass  $m$ , moving along the  $x$ -axis and with potential energy  $V$ .

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2m}{h^2} (E - V)\psi = 0. \quad (I, 17)$$

Substituting  $V = \frac{1}{2} kx^2$ , we obtain Schroedinger's equation for the harmonic oscillator. In this case only those values of the energy (eigenvalues) which are of the form

$$E = h\nu \left( v + \frac{1}{2} \right) \quad (I, 18)$$



where  $v = 1, 2, 3, 4, \dots$ , give a useful solution  $\psi$  which is single-valued, finite and continuous, and vanishes for  $x \rightarrow \infty$ . For the fact that the energy can take those discrete values only, the energy is said to be quantized and  $v$  is called the vibrational quantum number.

Equation (I, 18) shows that the energy levels are equidistant, i.e., differ by the same value. Also, in the lowest state  $v = 0$  there is still a vibrational energy  $\frac{1}{2} h\nu$  which is called the "zero-point energy" or "zero-point vibration." The

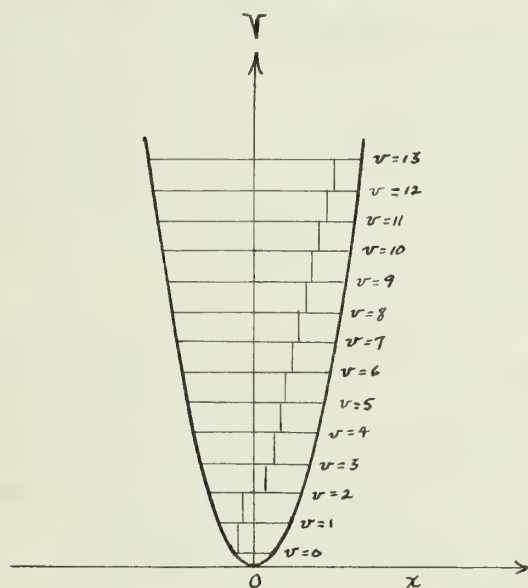


Fig. 4

different energy levels are represented by horizontal lines in Fig. 4. Emission or absorption of radiation takes place when the energy state of the oscillator is changed from one level to another. Not all transitions occur; the possible transitions are governed by selection rules. These rules are derived from the quantum mechanical calculation of the transition probabilities. The

selection rule for the harmonic oscillator allows only transitions for which  $\Delta v = \pm 1$ . In Fig. 4, the vertical lines from each level to the next one show these transitions. This selection rule holds for the infrared and the Raman spectrum as well. For a transition from any level  $v$  to  $v + 1$  the absorbed energy is





$$E = h\nu \left( \nu + \frac{3}{2} \right) - h\nu \left( \nu + \frac{1}{2} \right) = h\nu \quad (\text{I, 19})$$

where  $\nu$  is the frequency of the oscillator.

On substituting  $V = kx^2 + k_1x^3 + k_2x^4 + \dots$  in (I, 17) we have Schroedinger's equation for the anharmonic oscillator. In this case we obtain useful solutions only for energy values of the following form

$$E = h\nu \left( \nu + \frac{1}{2} \right) + x' \left( \nu + \frac{1}{2} \right)^2 + x'' \left( \nu + \frac{1}{2} \right)^3 + \dots \quad (\text{I, 20})$$

where the quantum number  $\nu$  takes again integral values. The constants  $x'$ ,  $x''$ , ... are called anharmonicity constants.  $\nu$  is the zero order frequency. Since

$$|x''| \ll |x'| \quad \text{and} \quad |x'''| \ll |x''|, \dots \quad (\text{I, 21})$$

terms containing  $x''$ ,  $x'''$ , ... can be neglected. In some cases  $x''$  can also be neglected in a good approximation.  $x'$  is practically always negative, so that for the same quantum number the energy of the harmonic oscillator is greater than that of the anharmonic oscillator. Equation (I, 20) shows that the energy levels are

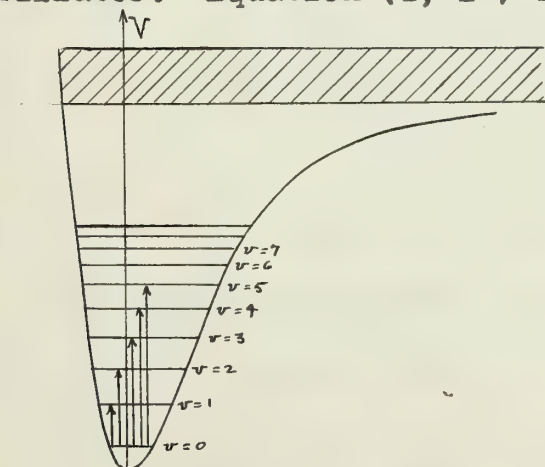


Fig. 5

not equidistant but draw closer together as we go to higher quantum numbers. The energy level diagram is shown in Fig. 5. The energy is not quantized beyond the dissociation energy so that after this level we have a continuum.



The selection rule for the anharmonic oscillator is

$$\Delta v = \pm 1, \pm 2, \pm 3, \dots$$

Transitions from the ground state  $v = 0$ , in the infrared absorption spectrum are represented by vertical lines in Fig. 5. The frequency absorbed in the first transition from  $v = 0$  to  $v = 1$ , is called the fundamental, and the frequencies of the other transitions are called 1-st, 2-nd, 3-rd, ... overtones, in analogy with classical theory, although these frequencies are not exact multiples of the fundamental.

In the Raman effect the selection rule for the anharmonic oscillator is also  $\Delta v = \pm 1, \pm 2, \dots$ . Therefore we expect here also the appearance of overtones. In both, infrared and Raman spectra, the intensity of the overtones is very much smaller than that of the fundamental and the higher the overtone considered the less its intensity.

The following notation will be used in what follows:

$\nu$  = frequency in vib/sec

$\omega$  = zero order frequency in vib/sec

$\bar{\nu}$  = frequency in  $\text{cm}^{-1}$

$\bar{\omega}$  = zero order frequency in  $\text{cm}^{-1}$

$x', x'', x''', \dots$  = anharmonicities in ergs

$x_1, x_2, x_3, \dots$  = " "  $\text{cm}^{-1}$

The frequency absorbed in a transition from  $v = 0$  to  $v = v$  is to a good approximation

$$\bar{\nu}_v = \bar{\omega} \left( v + \frac{1}{2} \right) + x_1 \left( v + \frac{1}{2} \right)^2 - \frac{1}{2} \bar{\omega} - \left( \frac{1}{2} \right)^2 x_1$$





$$\bar{\nu}_v = \bar{\omega}_v + x_1 v + x_1 v^2. \quad (\text{I, } 22)$$

For the fundamental,  $v = 1$  and

$$\bar{\nu}_{\text{fund}} = \bar{\omega} + 2x_1, \quad (\text{I, } 23)$$

Since  $x_1$  is almost always negative and small, the frequency of the fundamental is slightly less than the zero order frequency.

As mentioned before the vibrations of a polyatomic molecule are actually anharmonic. This is due to the fact that the potential of the field in a molecule is not a simple quadratic function of the displacements but contains terms of higher order. However, one can still associate a zero order frequency  $\omega_k$  with each vibration  $k$ . The zero order frequencies are given by the secular equation while the fundamentals are observed in the spectrum.

The solution of Schroedinger's equation for a vibrating polyatomic molecule shows that the energy can only take the values

$$\begin{aligned} \bar{E} = & \bar{\omega}_1(v_1 + \frac{1}{2}) + \bar{\omega}_2(v_2 + \frac{1}{2}) + \bar{\omega}_3(v_3 + \frac{1}{2}) + \dots \\ & + x_{11}(v_1 + \frac{1}{2})^2 + x_{22}(v_2 + \frac{1}{2})^2 + x_{33}(v_3 + \frac{1}{2})^2 \\ & + \dots + x_{12}(v_1 + \frac{1}{2})(v_2 + \frac{1}{2}) + x_{13}(v_1 + \frac{1}{2})(v_3 + \frac{1}{2}) \\ & + x_{23}(v_2 + \frac{1}{2})(v_3 + \frac{1}{2}) + \dots \end{aligned} \quad (\text{I, } 24)$$

where the  $x_{ij}$  are anharmonicity constants and the  $v_i$  are the quantum numbers.  $\bar{E}$  is of course in  $\text{cm}^{-1}$ .

In the case of one oscillator we obtained a relation (eq. I, 23)



between the fundamental and the zero order frequency in terms of the anharmonicity  $x_1$ . Similarly, we can obtain expressions for the fundamentals of the vibrations in a polyatomic molecule in terms of the zero order frequencies and the anharmonicities  $x_{1j}$ .

For example, let us consider a non-linear triatomic molecule which has  $3(3) - 6 = 3$  vibrations. For the fundamental  $\bar{\nu}_1$  of vibration 1, the transition is represented by  $v_1 = 0 \rightarrow v_1 = 1$  while the rest of the quantum numbers remain at a constant level, say  $v_2 = v_3 = 0$ . Therefore from (I, 24) we have,

$$\begin{aligned}\bar{\nu}_1 &= \bar{\omega}_1 \left(1 + \frac{1}{2}\right) + x_{11} \left(1 + \frac{1}{2}\right)^2 \\ &\quad + x_{12} \left(1 + \frac{1}{2}\right) \left(\frac{1}{2}\right) - \frac{1}{2} \bar{\omega}_1 - x_{11} \left(\frac{1}{4}\right) - \frac{1}{4} x_{12} \\ \bar{\nu}_1 &= \frac{3}{2} \bar{\omega}_1 + \frac{9}{4} x_{11} + \frac{9}{4} x_{13} + \frac{3}{4} x_{12} - \frac{1}{2} \bar{\omega}_1 - \frac{1}{4} x_{11} - \frac{1}{4} x_{12} - \frac{1}{4} x_{13} \\ \bar{\nu}_1 &= \bar{\omega}_1 + 2x_{11} + \frac{1}{2} x_{12} + \frac{1}{2} x_{13}. \quad (\text{I, 25})\end{aligned}$$

Similarly

$$\bar{\nu}_2 = \bar{\omega}_2 + 2x_{22} + \frac{1}{2} x_{12} + \frac{1}{2} x_{23}, \quad (\text{I, 26})$$

and

$$\bar{\nu}_3 = \bar{\omega}_3 + 2x_{33} + \frac{1}{2} x_{13} + \frac{1}{2} x_{23}. \quad (\text{I, 27})$$

Since the  $x_{1j}$  are usually negative and, in general, very small in absolute value, the observed fundamental frequencies  $\bar{\nu}_1$  are usually slightly less than the zero order frequencies  $\bar{\omega}_1$ . There are some molecules for which the zero order frequencies



have been calculated. In other cases this has not been done because of lack of experimental data. The zero order frequencies can be replaced in many cases by the fundamentals to a fairly good degree of approximation. However, in other cases this substitution leads to wrong conclusions.

The relation mentioned before with reference to the isotope effect, and which will be discussed later in this thesis, has been derived for the zero order frequencies.





## Chapter 2

### SYMMETRY CONSIDERATIONS

#### 1. Point Groups.

Consider a molecule with its atoms in their equilibrium positions, having a certain configuration. If we subject this molecule to a certain operation as for example, a rotation about an axis or a reflection at a plane, and the resulting configuration is indistinguishable from the original one the molecule is said to be symmetric with respect to that particular operation. The operation is called a symmetry operation or a transformation. A symmetry operation is carried out with respect to an element of symmetry in the molecule. An element of symmetry may be a plane, a straight line or axis, or a point. Elements of symmetry go through or lie within the molecule. Planes which are symmetry elements are denoted by  $\sigma$ . (See Fig. 6.) If the configuration is the same when the molecule has rotated about an axis by an angle  $2\pi/p$ , this axis is called a  $p$ -fold axis of symmetry. (See Fig. 7.) When a point is a symmetry element, it is called center of symmetry. The point  $i$  is a center of symmetry, if for each atom  $k$  there is another atom  $j$  so that  $i$  bisects the line joining  $k$  and  $j$ . The symmetry operation connected with the center of



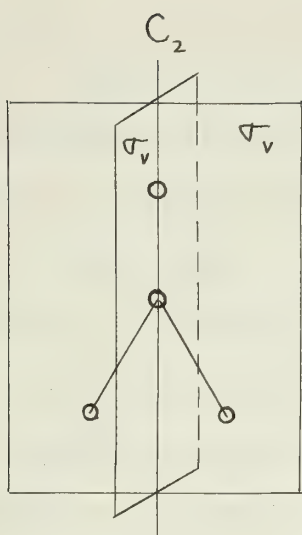


Fig. 6.

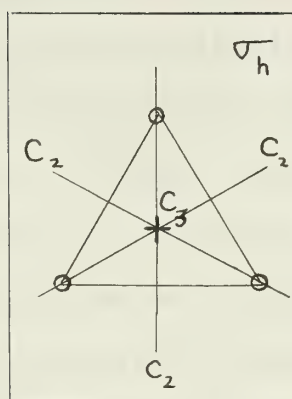


Fig. 7

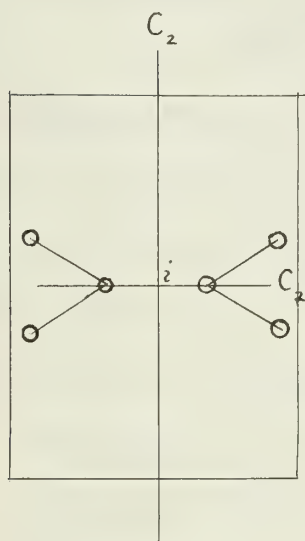


Fig 8

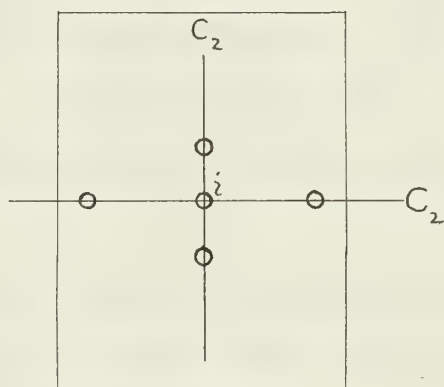


Fig. 9

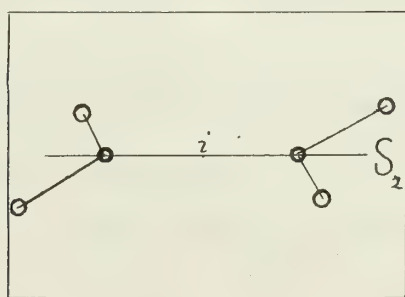


Fig. 10

Fig. 6 to Fig. 10 show the following symmetry elements:  $C_p$  = p-fold axis of symmetry,  $\sigma_v$  = plane of symmetry containing the axis of higher symmetry,  $\sigma_h$  = plane of symmetry  $\perp$  to the axis of higher symmetry,  $i$  = center of symmetry  $S_p$  = p-fold rotation reflection axis. + in Fig. 7 means an axis  $C_3$  to the paper.  $I$  = identity.





symmetry is inversion or reflection at the center; it corresponds to an interchange of all atoms  $k$  and  $j$ , or to a multiplication of the coordinates of all atoms by  $-1$ , when the origin of coordinates is at the point  $i$ . A molecule may or may not have an atom at the center of symmetry. (See Figs. 8 and 9.) Another element of symmetry is the  $p$ -fold rotation reflection axis. The corresponding symmetry operation consists of a rotation by an angle  $2\pi/p$  followed by a reflection at a plane perpendicular to the axis of rotation (see Fig. 10). The identity symmetry operation consists in leaving the molecule unchanged, and it is introduced only for mathematical purposes. All molecules, obviously, are symmetric with respect to the identity. The notation used to indicate the different symmetry elements is given together with the figures 6-10.

Some symmetry elements in a molecule imply the existence of others. For example, a 2-fold rotation reflection axis implies a center of symmetry. (See Fig. 10.) Symmetry elements can thus be classified as essential symmetry elements and non-essential symmetry elements. Non-essential elements can be derived from the essential ones.

Consider a compatible set of symmetry operations which leaves at least one point unchanged in the molecule, and which is such that the successive application of any two of these symmetry operations is equivalent to a symmetry operation belonging to the same set. Then the set of symmetry operations is called a point group. The following table includes some of the point groups



and the corresponding notation used when referring to them\*.

Table I.

Point Groups	Symmetry Elements
$C_1$	No symmetry
$C_2$	One $C_2$
$C_s$	One $\sigma$
$C_i \equiv S_2$	1 ( $\equiv S_2$ )
$C_{2v}$	One $C_2$ , two $\sigma_v$
$C_{3v}$	One $C_3$ , three $\sigma_v$
$D_2 \equiv V$	Three $C_2$ (mutually perpendicular)
$D_{2h} \equiv V_h$	Three $C_2$ (mutually perpendicular), three $\sigma$ (mutually perpendicular), 1
$D_{\infty h}$	$C_{\infty}$ , $\infty$ number of $C_2$ (perpendicular to $C_{\infty}$ ), $\infty$ number of $\sigma_v$ , one $\sigma_h$ $C_p$ and $S_p$ coincident with $C_{\infty}$ , 1

In Figs. 11 and 12 are shown two molecules which are examples of point groups  $C_{2v}$  and  $D_{\infty h}$  respectively. The first molecule is seen to have a two fold axis  $C_2$  and two symmetry planes  $\sigma_v$ , and no more symmetry elements. Therefore it belongs to the point

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\* The notation used for the point groups in molecular structure is the same as that introduced by Schoenflies in the theory of crystal structure.



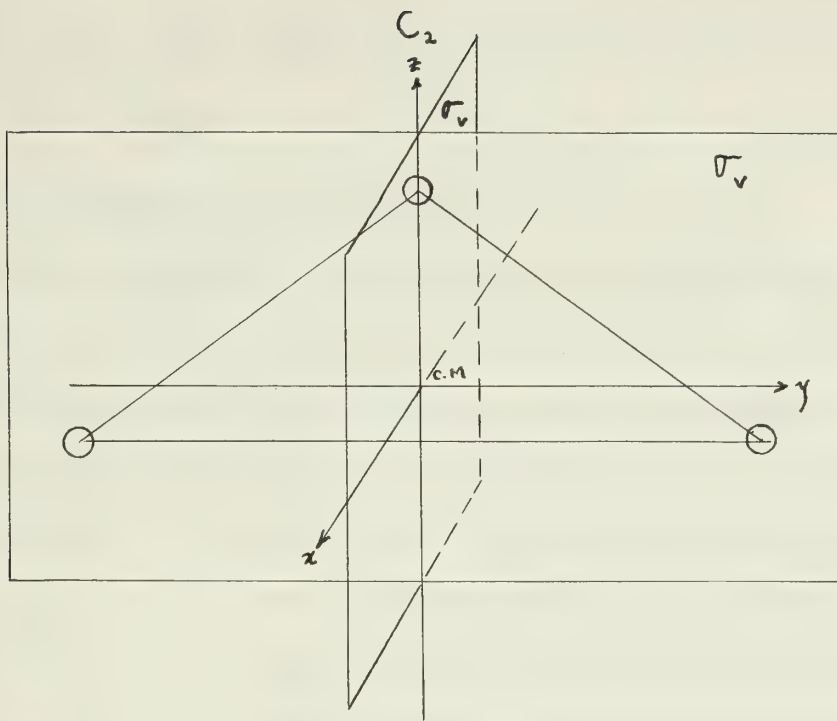


Fig. 11

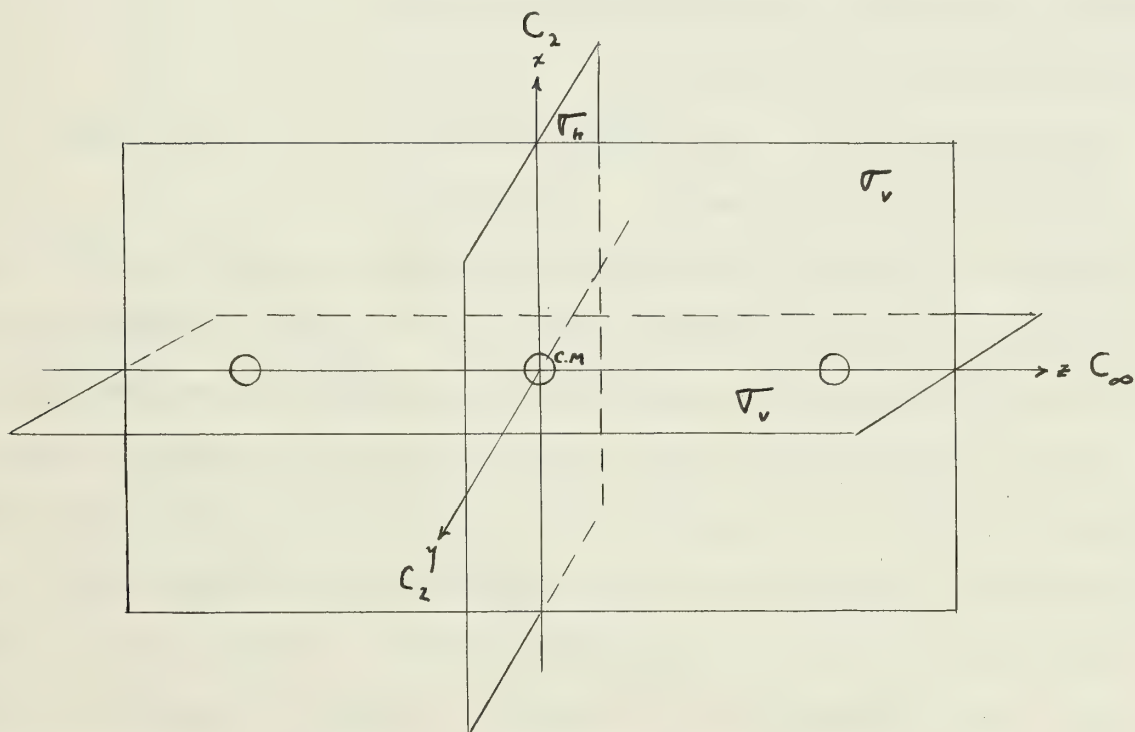


Fig. 12





group  $C_{2v}$ . Similarly, the second molecule is seen to belong to the point group  $D_{\infty h}$ .

## 2. Symmetry Properties of Vibrations.<sup>3,4,5</sup>

Consider a molecule at any instant during a normal vibration. The vibration need not be symmetric with respect to the symmetry operations permitted by the molecule while in equilibrium. As an example Fig. 13 shows one of the vibrations of the bent symmetrical  $XY_2$  molecule. This vibration is not symmetric with respect

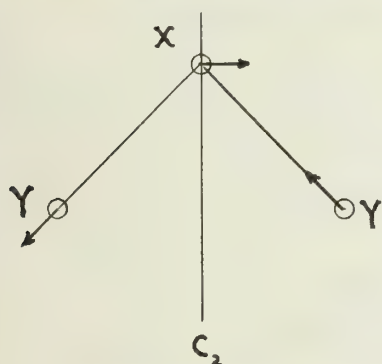


Fig. 13

to a rotation about  $C_2$ , while it is symmetry with respect to a reflection in the molecular plane. In order to study the behaviour of the vibrations with respect to the symmetry operations permitted by the molecule we classify the different vibrations as degenerate and non-degenerate vibrations. If two or more vibrations

happen to have the same frequency, we have a two-fold or higher-fold degeneracy, respectively. The vibrations whose frequencies coincide are called degenerate vibrations. They are referred to as doubly degenerate vibrations when only two coincide, triply degenerate when three coincide, etc. Degeneracies come in when two or more roots of the secular equation are equal. Under this condition the system of equations (I, 13) has two or more independent solutions<sup>6</sup>, which correspond to two or more normal vibrations of the same frequency. Consider the case of a double degeneracy. The set of coordinates  $x_1^a, y_1^a, z_1^a, x_2^a, y_2^a, z_2^a, \dots$  which constitutes a first solution is represented by the normal



coordinate  $\xi^a$ , and the set of coordinates  $x_1^b, y_1^b, z_1^b, x_2^b, y_2^b, z_2^b, \dots$  which constitutes a second solution, is represented by the normal coordinate  $\xi^b$ . Since (I, 13) is a homogeneous system of equations, any linear combination of the previous solutions  $(dx_1^a + ex_1^b, dy_1^a + ey_1^b, dz_1^a + ez_1^b, dx_2^a + ex_2^b, \dots)$  is also a solution. This means that actually a double degeneracy implies for the same frequency, the existence of an infinite number of vibrations which can be represented by the normal coordinates  $d\xi^a + \xi^b$ . In the case of a triple degeneracy, there is, for the same frequency, an infinite number of vibrations which can be represented by linear combinations of three independent normal vibrations:  $d\xi^a + e\xi^b + f\xi^c$ .

Vibrations which are not degenerate are called non-degenerate vibrations. Let us consider first the behaviour of non-degenerate vibrations with respect to the symmetry operations which are defined for the molecule in its equilibrium position. Since the equilibrium configuration of the molecule is not changed with the symmetry operation, the force constants remain also unchanged. Therefore, after the vibrating molecule is transformed, the new displacements of all atoms along the three coordinate axes  $(\bar{x}_1, \bar{y}_1, \bar{z}_1, \bar{x}_2, \dots, \bar{z}_N)$  have to satisfy the same system of equations (I, 13) that held before the symmetry operation was carried out. Since (I, 13) is a homogeneous system, its solution gives the ratios

$$\frac{x_1}{y_1}, \frac{y_1}{z_1}, \frac{z_1}{x_2}, \frac{x_2}{y_2}, \dots$$





For these ratios to stay the same, the coordinates  $x_1, y_1, z_1, x_2, y_2, z_2, \dots$  can only either stay the same, or all change sign\*. If  $\xi$  and  $\bar{\xi}$  are respectively the normal coordinates before and after the symmetry operation is performed, we can say that either

$$\bar{\xi} = \xi \quad \text{or} \quad \bar{\xi} = -\xi. \quad (\text{II}, 1)$$

If  $\bar{\xi} = \xi$  holds, the vibration is said to be symmetric with respect to that particular symmetry operation, while if  $\bar{\xi} = -\xi$  holds, the vibration is said to be antisymmetric. A non-degenerate vibration can only be symmetric or antisymmetric with respect to symmetry operations permitted by the molecule. This is expressed by writing +1 or -1 for each symmetry element in the molecule. (See Table 2.)

In the case of degenerate vibrations the situation is different. If the vibration is doubly degenerate there are two sets of vibrations with normal coordinates  $\xi^a$  and  $\xi^b$  that are solutions of (I, 13) for the same value of  $\nu$ . Moreover, any linear combination  $d\xi^a + e\xi^b$  is also a solution. When the molecule executing vibration  $\xi^a$  is transformed, the new set of coordinates of the vibration has to satisfy the same system (I, 13) because the force constants and the masses are the same. This is

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\* Since the transformation of the molecule is carried out at a certain instant during the vibration the possibility that all displacements be multiplied by a constant  $c$  such that  $|c| \neq 1$  is excluded.



fulfilled, in the more general case, when the transformed vibration  $\bar{\xi}^a$  is a linear combination of  $\xi^a$  and  $\xi^b$ , i.e.,

$$\bar{\xi}^a = d_{aa} \xi^a + d_{ab} \xi^b. \quad (\text{II}, 2)$$

In a similar way, if the molecule is executing the vibration represented by  $\xi^b$  when the symmetry operation is carried out, the resulting normal coordinate  $\bar{\xi}^b$  is in general a linear combination of  $\xi^a$  and  $\xi^b$ .

$$\bar{\xi}^b = d_{ba} \xi^a + d_{bb} \xi^b. \quad (\text{II}, 3)$$

Equations (II, 1) are seen to be a special case of (II, 2), namely, when  $d_{aa} = \pm 1$  and  $d_{ab} = 0$ . In particular cases a degenerate vibration may behave according to one of the transformations (II, 1), but not in the more general case. Relations similar to (II, 2) and (II, 3) hold also for triply degenerate vibrations.

In the case of a rotation about a  $p$ -fold axis of symmetry, doubly degenerate vibrations follow the transformation:

$$\begin{aligned} \bar{\xi}^a &= \xi^a \cos \varphi + \xi^b \sin \varphi \\ \bar{\xi}^b &= -\xi^a \sin \varphi + \xi^b \cos \varphi \end{aligned} \quad (\text{II}, 4)$$

where  $\varphi = \pm \frac{2\pi}{p} j$  and  $j = 1, 2, 3, \dots, (p - 1)$ .

The behaviour of doubly degenerate vibrations is described by giving for all symmetry operations in the molecule the values of the sum

$$\chi = d_{aa} + d_{bb} \quad (\text{II}, 5)$$



where  $d_{aa}$  and  $d_{bb}$  are the constants appearing in the transformation equations (II, 2) and (II, 3) for doubly degenerate vibrations. For triply degenerate vibrations the values of  $\chi = d_{aa} + d_{bb} + d_{cc}$  are given. The sums  $\chi$  are called characters. In the case of non-degenerate vibrations it was seen that the characters are either +1 or -1.

For the same vibration, the values of the characters corresponding to the different symmetry operations are in general different. For example, a non-degenerate vibration can be symmetric with respect to a reflection at a plane  $\sigma$  but antisymmetric with respect to a rotation about a  $C_p$  axis. Then, for that vibration,  $\chi^\sigma = +1$  while  $\chi^{C_p} = -1$ .

If a value  $\chi$  is assigned to each of the symmetry operations permitted by the molecule such that the resulting combination is compatible, the set of values  $\chi$  is called a species or a symmetry type. In group theory it is called an irreducible representation of the group.<sup>7,8</sup> The symmetry types represent combinations of symmetry properties of the normal vibrations and of the vibrational eigenfunctions. In general, there are several possible symmetry types for the same molecule. The vibrations of a molecule are distributed among the different species compatible with the point group to which the molecule belongs.

Tables have been collected<sup>9,10,11,1</sup> for the different point groups, containing the symmetry types of vibrations characteristic of a particular group, and the characters corresponding to the different symmetry operations. The symbols used for classifying the different species follow Placzek's notation.<sup>9</sup> In the





mentioned tables the characters are given for the essential symmetry elements of the group, and sometimes, for completeness, the characters of the non-essential symmetry elements are also included. In making these tables, the origin of coordinates is placed at the center of mass of the molecule, and the z-axis along the axis of highest symmetry. Also the coordinates x, y, z form a right-handed system. (See Figs. 11 and 12.) Since here we will deal with the point groups  $C_{2v}$  and  $D_{\infty h}$ , tables for these point groups are included in this section.

Table 2.

 $C_{2v}$ 

Symmetry Elements Species	I	$C_2(z)$	$\sigma_{xz}$	$\sigma_{yz}$	
$A_1$	+1	+1	+1	+1	$T_z$
$A_2$	+1	+1	-1	-1	$R_z$
$B_1$	+1	-1	+1	-1	$T_x R_y$
$B_2$	+1	-1	-1	+1	$T_y, R_x$

The column at the left of the above table indicates the different species, and the upper row shows the different symmetry elements of the group. Since there are no degenerate vibrations for this point group the characters are always either +1 or -1. For species  $A_1$  all the characters are +1; for this reason, vibrations belonging to species  $A_1$  are called totally symmetric vibrations. Vibrations belonging to  $A_2$  are symmetric with respect to



rotation about  $C_2(z)$ , while antisymmetric with respect to reflection at the planes  $\sigma_{xz}$  and  $\sigma_{yz}$ . In a similar way the behaviour of vibrations  $B_1$  and  $B_2$  can be read from the table. The letters A and B represent, respectively, symmetry and antisymmetry with respect to the axis of higher symmetry, and the subscripts 1 and 2 represent, in this case, symmetry and antisymmetry with respect to the plane  $\sigma_{xz}$ . The non-genuine vibrations, i.e., rotations and translations, can be classified in the same way as genuine vibrations. The right-hand column of the table shows to which symmetry type these translations and rotations belong.  $T_z$  means translation along the z-axis,  $R_x$  means rotation about the x-axis, etc.

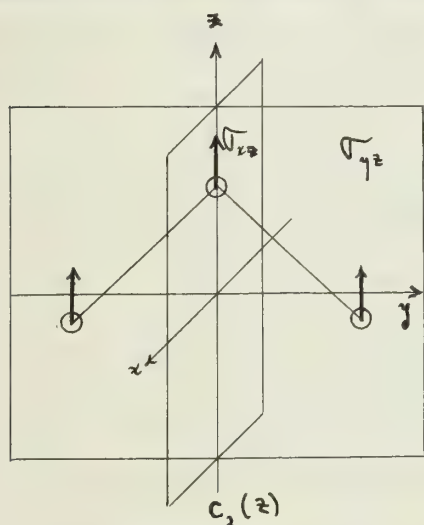


Fig. 14

Fig. 14 represents the translation along the z-axis of a molecule belonging to the point group  $C_{2v}$ . It is seen that this translation is symmetric with respect to a rotation about  $C_2(z)$ , reflection at  $\sigma_{xz}$  and  $\sigma_{yz}$ , and of course with respect to the identity I. Therefore  $T_z$  belongs to species  $A_1$ .

Similarly we can verify the species of the rest of the non-genuine vibrations.

In order to determine the number of vibrations of each species in a molecule, the atoms may be divided in sets of equivalent nuclei. With the purpose of defining a set of equivalent nuclei we will say that atoms belonging to the same set can be transformed into one another by performing the different symmetry





operations of the molecule. Any one of the members of a set is called the representative nucleus of that set. For the non-degenerate vibrations the positions of the members of a set are fixed when the position of the representative nucleus is fixed. If the representative nucleus does not lie in any symmetry element it has three degrees of freedom. Therefore the set has three degrees of freedom itself. If the representative nucleus lies on some symmetry element it has less than three degrees of freedom, and the corresponding set contributes less than three vibrations to a certain species. The number of vibrations that a set of nuclei contributes to a symmetry type is equal to the number of degrees of freedom of that set in relation to the particular species. As an example we may consider point group  $C_{2v}$ . If there are  $n$  sets of atoms with their representative nuclei in no symmetry element, they contribute  $3n$  vibrations to any species. If there are  $n_{xz}$  sets whose representative nuclei lie in the plane  $xz$ , they have to move in the plane  $xz$  in the  $A_1$  and  $B_1$  vibrations, and perpendicular to it in the  $A_2$  and  $B_2$  vibrations, since  $A_1$  and  $B_1$  vibrations are symmetric with respect to a reflection at that plane, while  $A_2$  and  $B_2$  vibrations are antisymmetric with respect to a reflection at that plane. This means that the sets  $n_{xz}$  have 2 degrees of freedom in relation to species  $A_1$  and  $B_1$  but only one degree of freedom in relation to species  $A_2$  and  $B_2$ . Therefore, these  $n_{xz}$  sets contribute  $2n_{xz}$  vibrations to species  $A_1$  and to species  $B_1$ , and  $n_{xz}$  vibrations to species  $A_2$  and  $B_2$ . Similarly, if  $n_{yz}$  is the number of sets whose representative nuclei lie in the  $yz$  plane, they contribute  $2n_{yz}$  vibrations



to species  $A_1$  and  $B_2$ , and  $n_{yz}$  vibrations to species  $A_2$  and  $B_1$ . If the representative nucleus lies on all symmetry elements it constitutes a set by itself. In order that the motion of such a nucleus be symmetric with respect to all elements of symmetry it has to take place along the  $C_2$  axis, i.e., it has one degree of freedom. Therefore, if there are  $n_0$  nuclei of this kind they contribute  $n_0$  vibrations to species  $A_1$ . They do not contribute any vibration to species  $A_2$  because an atom lying in both planes of symmetry cannot move antisymmetrically (i.e., perpendicular) with respect to both planes at the same time. (This is equivalent to 0 degrees of freedom.) The  $n_0$  atoms contribute  $n_0$  vibrations to species  $B_1$  and  $B_2$  because in order that the motion be antisymmetric with respect to one plane and symmetric with respect to a second plane which is perpendicular to the first, the motion must be perpendicular to the first plane; i.e., each atom has one degree of freedom in each case. These conclusions for point group  $C_{2v}$  are given in Table 3, which includes genuine and non-genuine vibrations.

Table 3.

Species	Sets				Total number of vibrations including genuine and non-genuine vibrations
	$n$	$n_{xz}$	$n_{yz}$	$n_0$	
$A_1$	$3n$	$2n_{xz}$	$2n_{yz}$	$n_0$	$3n + 2n_{xz} + 2n_{yz} + n_0$
$A_2$	$3n$	$n_{xz}$	$n_{yz}$	0	$3n + n_{xz} + n_{yz}$
$B_1$	$3n$	$2n_{xz}$	$n_{yz}$	$n_0$	$3n + n_{xz} + n_{yz} + n_0$
$B_2$	$3n$	$n_{xz}$	$2n_{yz}$	$n_0$	$3n + n_{xz} + 2n_{yz} + n_0$





It was shown in Table 2 to which species translations and rotations belong. These non-genuine vibrations must be subtracted from the expressions given in the last row of Table 3 in order to obtain the number of genuine vibrations of each species.

As an example, the number of vibrations belonging to each species will be calculated now for the bent triatomic  $XY_2$  molecule of point group  $C_{2v}$ . This molecule is shown in Fig. 11. From the figure it can be seen that  $n = 0$ ,  $n_{xz} = 0$ ,  $n_{yz} = 1$ , and  $n_o = 1$ . Substituting these values in the expressions of the last row in Table 3 we obtain 3 vibrations of species  $A_1$ , 1 vibration of species  $A_2$ , 2 of species  $B_1$  and 3 of species  $B_2$ . From Table 2,  $T_z$  belongs to  $A_1$ ,  $R_z$  belongs to  $A_2$ ,  $T_x$  and  $R_y$  belong to  $B_1$ , and  $T_y$  and  $R_x$  belong to  $B_2$ . By subtracting these six non-genuine vibrations from the total number already calculated for each species we obtain the following genuine vibrations for this molecule: two  $A_1$  vibrations,  $\omega_1$  and  $\omega_2$ , no  $A_2$  vibrations, no  $B_1$  vibrations and one  $B_2$  vibration,  $\omega_3$ . These vibrations are shown in Fig. 15.

Tables similar to the ones just discussed are included for the point group  $D_{\infty h}$ ; see Tables 4 and 5. Because of the presence of the  $C_{\infty}$  axis, this point group has degenerate vibrations and therefore characters different from  $\pm 1$  appear in Table 4. The notation used for the symmetry types of this point group is the same as that used for the electronic states in diatomic molecules. The  $\Sigma$ 's are used for the non-degenerate vibrations;  $\Pi$ 's,  $\Delta$ 's, ... are used for degenerate vibrations. g and u imply symmetry and antisymmetry with respect to the center of symmetry, respectively; the superscripts + and - of the  $\Sigma$ 's mean symmetry and





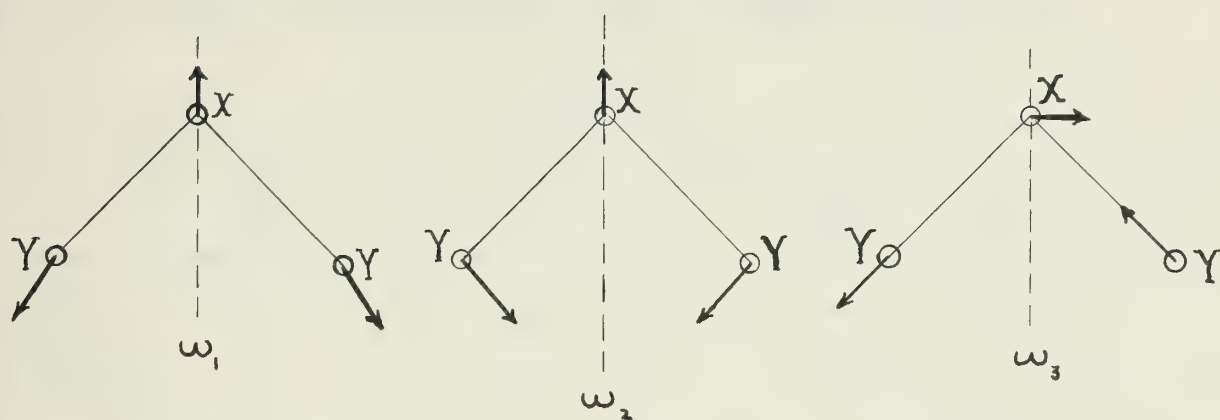


Fig. 15

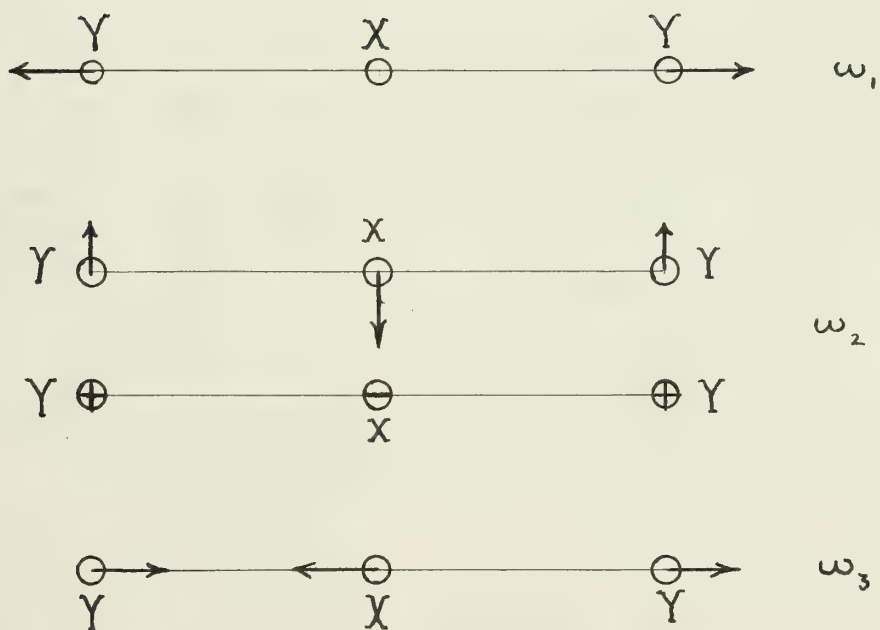


Fig. 16



and antisymmetry with respect to the infinite number of planes  $\sigma_v$ . In Table 5,  $n_\infty$  is the number of sets lying in  $C_\infty$ , and  $n_0$  is the number of nuclei lying in all elements of symmetry.

Table 4.

	I	$2C_\infty'$	$\sigma_h$	$\infty C_2$	$\infty \sigma_v$	$2S_\infty'$	$S_2=1$	
$\Sigma_g^+$	+1	+1	+1	+1	+1	+1	+1	
$\Sigma_u^+$	+1	+1	-1	-1	+1	-1	-1	$T_z$
$\Sigma_g^-$	+1	+1	+1	-1	-1	+1	+1	$R_z$
$\Sigma_u^-$	+1	+1	-1	+1	-1	-1	-1	
$\Pi_g$	+2	$2 \cos \varphi$	-2	0	0	$-2 \cos \varphi$	+2	$R_x, R_y$
$\Pi_u$	+2	$2 \cos \varphi$	+2	0	0	$+2 \cos \varphi$	-2	$T_x, T_y$
$\Delta_g$	+2	$2 \cos 2\varphi$	+2	0	0	$+2 \cos 2\varphi$	+2	
$\Delta_u$	+2	$2 \cos 2\varphi$	-2	0	0	$-2 \cos 2\varphi$	-2	
$\Phi_g$	+2	$2 \cos 3\varphi$	-2	0	0	$-2 \cos 3\varphi$	+2	
$\Phi_u$	+2	$2 \cos 3\varphi$	+2	0	0	$+2 \cos 3\varphi$	-2	
...	..	.....	..	..	..	.....	..	





Table 5.

$D_{\infty h}$ Species	Total number of genuine vibrations
$\sum_g^+$	$n_{\infty}$
$\sum_u^+$	$n_{\infty} + n_0 - 1$
$\sum_g^-, \sum_u^-$	0
$\pi_g$	$n_{\infty} - 1$
$\pi_u$	$n_{\infty} + n_0 - 1$
$\Delta_g, \Delta_u, \phi_g, \phi_u$	0

For the linear symmetrical triatomic molecule  $XY_2$  shown in Fig. 12,  $n_{\infty} = 1$  and  $n_0 = 1$ . From Table 5 it then follows that this molecule has one genuine vibration,  $\omega_1$ , of species  $\sum_g^+$ , one genuine vibration,  $\omega_3$ , of species  $\sum_u^+$  and one genuine doubly-degenerate vibration,  $\omega_2$ , of species  $\pi_u$ . These vibrations are shown in Fig. 16. The + and - in vibration  $\omega_2$  mean motions perpendicular to the paper in opposite directions.



## Chapter 3

### THE ISOTOPE EFFECT

#### 1. The Redlich-Teller Product Rule.

It has been mentioned before that the vibrational frequencies of a molecule change with isotopic substitutions. The secular equation shows that the zero-order frequencies of the vibrations depend on the masses of the atoms and on the force constants. When the atoms of a molecule are substituted by isotopes, the force constants remain the same, but since the masses are slightly different the frequencies of the isotopic molecule are shifted with respect to those of the ordinary molecule. For each species of vibrations of a molecule, there is an expression which relates all the frequencies of that species with the corresponding isotopic frequencies. The relation is known as the Redlich-Teller product rule<sup>12,13</sup> and it holds strictly only for the zero-order frequencies. In words, the rule states that if  $\omega_1, \omega_2, \omega_3, \dots, \omega_f$  are the zero-order frequencies of the  $f$  vibrations of any species  $S$  in a molecule, and if  $\omega_1^1, \omega_2^1, \omega_3^1, \dots, \omega_f^1$  are the corresponding zero-order frequencies of the isotopic molecule, then the product  $\prod_{j=1}^f \frac{\omega_j^1}{\omega_j}$  is independent of the force constants



and depends only on the masses of the atoms and on the geometry of the molecule. In order to state the mathematical expression of the rule, for any species S, the following notation will be employed:

$t$  = number of translations belonging to species S

$m_k$  = mass of the representative nucleus of set k

$\beta_k$  = number of vibrations contributing to species S by set k of equivalent nuclei. (The  $\beta_k$ 's are the coefficients of the n's in Tables 3 and 5.)

$M$  = total mass of the molecule

$I_x, I_y, I_z$  = moments of inertia of the molecule about the x, y, z-axes, respectively\*.

$\delta_x = 1$ , if rotation about the x-axis belongs to species S

$\delta_x = 0$ , if rotation about the x-axis does not belong to species S

$\delta_y$  and  $\delta_z$  are, similarly, 1 or 0 according to whether rotation about the y and z axes belongs to species S or not.

The product rule states that

$$\prod_{j=1}^f \frac{\omega_j^1}{\omega_j} = \left[ \prod_{k=1}^k \left( \frac{m_k}{m_1} \right)^{\beta_k} \left( \frac{M}{M} \right)^t \left( \frac{I_x^1}{I_x} \right)^{\delta_x} \left( \frac{I_y^1}{I_y} \right)^{\delta_y} \left( \frac{I_z^1}{I_z} \right)^{\delta_z} \right]^{1/2} \quad (\text{III, 1})$$

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\* The position of the system of coordinates x, y, z with respect to the molecule is the same as that described on page 31 for the construction of the referred tables in section 2, Chapter 2.





where the quantities having a superscript 1 refer to the isotopic molecule, while those having no superscript refer to the ordinary molecule. O. Redlich has given a theoretical derivation for the rule<sup>12</sup> on the basis that the force constants remain the same with the substitution of isotopes.

Since the fundamental frequencies differ by small quantities only from the zero-order frequencies, the  $\omega$ 's in the product rule may sometimes be substituted by the fundamentals  $\nu$ 's. However, there are cases where this cannot be done, as will be pointed out in an example.

## 2. Application of the product rule to $XY_2$ molecules of point group $C_{2v}$ and to $XY_2$ molecules of point group $D_{\infty h}$ .

Let us apply the product rule to the non-linear symmetrical triatomic molecule  $XY_2$  of group  $C_{2v}$ . In the preceding chapter it was shown that this molecule has two vibrations  $\omega_1$  and  $\omega_2$  of species  $A_1$ , and one vibration  $\omega_3$  of species  $B_2$ . For species  $B_2$  the left-hand side of the product rule is  $\omega_1^1/\omega_3$ . We calculate

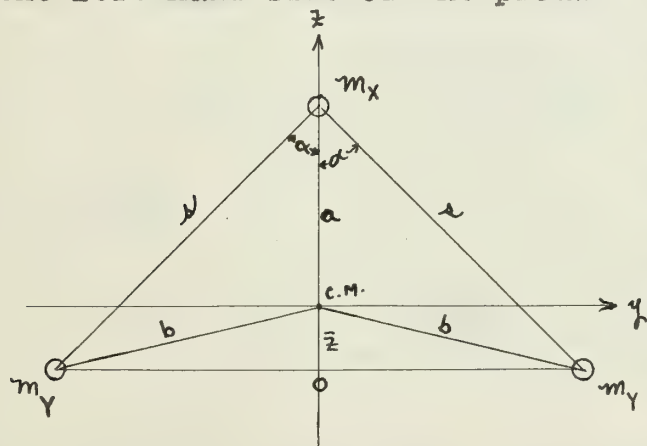


Fig. 17

now the right-hand side. There are two sets of equivalent nuclei with representative masses  $m_X$  and  $m_Y$ . Table 3 shows that in this case  $\beta_X = 1$  and  $\beta_Y = 2$ . Table 2 shows that  $t = 1$ , and  $\delta_X = 1$  and  $\delta_Y = \delta_Z = 0$  since the only rotation belonging to species  $B_2$  is a



rotation about the x-axis. Thus, the only moments of inertia appearing in the product rule are  $I_x$  and  $I_x^1$ . From Fig. 17

$$I_x = m_X a^2 + 2m_Y b^2. \quad (\text{III}, 2)$$

In order to calculate  $a$  and  $b$  we must know the position of the center of mass. The distance  $\bar{z}$  from the center of mass (C.M.) to the point  $O$  in Fig. 17 is

$$\bar{z} = \frac{m_X z_X + 2m_Y z_Y}{2m_Y + m_X} = \frac{m_X s \cos \alpha}{m_X + 2m_Y}. \quad (\text{III}, 3)$$

From the figure

$$\begin{aligned} a &= s \cos \alpha - \bar{z}, \\ b &= \sqrt{(s \sin \alpha)^2 + \bar{z}^2}. \end{aligned} \quad (\text{III}, 4)$$

Substituting these expressions in (III, 2) and taking account of (III, 3), we obtain

$$I_x = \frac{2m_Y m_X s^2 \cos^2 \alpha}{m_X + 2m_Y} + 2m_Y s^2 \sin^2 \alpha. \quad (\text{III}, 5)$$

Similarly

$$I_x^1 = \frac{2m_Y^1 m_X^1 s^2 \cos^2 \alpha}{m_X^1 + 2m_Y^1} + 2m_Y^1 s^2 \sin^2 \alpha. \quad (\text{III}, 6)$$

By taking the ratio  $I_x^1/I_x$  the quantity  $2s^2$  cancels out. Therefore,





$$\frac{I_X^1}{I_X} = \frac{m_Y^1}{m_Y} \frac{m_X^1 + 2m_Y^1 \sin^2 \alpha}{m_X + 2m_Y \sin^2 \alpha} \frac{M}{M^1}. \quad (\text{III}, 7)$$

Substituting in (III, 1) we obtain

$$\frac{\omega_3^1}{\omega_3} = \sqrt{\frac{m_X m_Y m_X^1 + 2m_Y^1 \sin^2 \alpha}{m_X^1 m_Y^1 m_X + 2m_Y \sin^2 \alpha}}. \quad (\text{III}, 8)$$

From this equation, the zero-order frequency  $\omega_3^1$  of the isotopic molecule can be calculated directly from the zero-order frequency  $\omega_3$  of the ordinary molecule. Since the fundamental frequencies,  $\nu_3$  and  $\nu_3^1$ , differ by a very small amount from the zero-order frequencies  $\omega_3$  and  $\omega_3^1$ , they may be used in the product rule for the calculation of  $\nu_3^1$  in terms of  $\nu_3$ . However, we cannot substitute the observed  $\nu_3$  and  $\nu_3^1$  for  $\omega_3$  and  $\omega_3^1$  in the product rule with the purpose of calculating the angle  $\alpha$ . Although the change in the value of the radical in (III, 8) is small when the  $\nu$ 's are substituted for the  $\omega$ 's,  $\alpha$ , calculated in this way, is very far from the actual value of the angle, since an angle is so sensitive to a change of its sine. Sometimes this interchange of  $\nu$ 's for  $\omega$ 's in the product rule leads to  $\sin \alpha > 1$ , which corresponds to an imaginary angle.

For vibrations  $\omega_1$  and  $\omega_2$  of species  $A_1$ ,  $\delta_x = \delta_y = \delta_z = 0$ , since there are no rotations belonging to this species, as may be seen from Table 2. Thus, the moments of inertia do not appear in the product rule and the radical is independent of the angle  $\alpha$ . Table 2 shows that  $t = 1$ , and Table 3 shows that  $\beta_X = 1$



and  $\beta_Y = 2$ . Therefore, the product rule for species  $A_1$  is

$$\frac{\omega_1^1}{\omega_1} \frac{\omega_2^1}{\omega_2} = \sqrt{\left(\frac{m_Y}{m_Y^1}\right)^2 \left(\frac{m_X}{m_X^1}\right) \frac{2m_Y^1 + m_X^1}{2m_Y + m_X}}. \quad (\text{III}, 9)$$

Let us consider next the product rule for linear symmetrical triatomic molecules  $XY_2$  of point group  $D_{\infty h}$ . Again, we have two sets of equivalent nuclei with representative masses  $m_X$  and  $m_Y$ . It was shown in the last chapter that there is only one vibration of species  $\Sigma_g^+$ , one of species  $\Sigma_u^+$  and one of species  $\Pi_u$ . Table 4 shows that the translation  $T_z$  belongs to  $\Sigma_u^+$ , and  $T_x$  and  $T_y$  belong to  $\Pi_u$ . The rotations do not belong to any of the species  $\Sigma_g^+$ ,  $\Sigma_u^+$  or  $\Pi_u$ . Therefore, for the three species  $\delta_x = \delta_y = \delta_z = 0$ .

Let us consider the product rule for vibration  $\omega_1$  of species  $\Sigma_g^+$ . From Table 5 it can be seen that  $\beta_X = 0$  and  $\beta_Y = 1$ .  $t = 0$  as shown in Table 4. On substituting in (III, 1) we obtain

$$\frac{\omega_1^1}{\omega_1} = \sqrt{\frac{m_Y}{m_Y^1}}. \quad (\text{III}, 10)$$

For vibrations  $\omega_2$  and  $\omega_3$  of species  $\Pi_u$  and  $\Sigma_u^+$  respectively,  $\beta_X = 1$  and  $\beta_Y = 1$  as shown in Table 5. According to Table 4  $t = 1$  for species  $\Sigma_u^+$ . Since  $T_x$  and  $T_y$  are degenerate with each other,  $t$  is also 1 for species  $\Pi_u$ . By substituting in (III, 1) we obtain for both species



$$\frac{\omega_2^1}{\omega_2} = \frac{\omega_3^1}{\omega_3} = \sqrt{\frac{\frac{m_X}{m_X^1} \quad \frac{m_Y}{m_Y^1} \quad \frac{2m_Y^1 + m_X^1}{2m_Y + m_X}}{}}. \quad (\text{III}, 11)$$

If only the center atom is substituted by an isotope in either the linear or the non-linear molecule, the effect is called center isotope effect, and relations (III, 8), (III, 9), (III, 10) and (III, 11) hold in which  $m_Y = m_Y^1$ . If only the end atoms Y are substituted by isotopes in either molecule, the effect is called end isotope effect and expressions (III, 8), (III, 9), (III, 10) and (III, 11) hold in which  $m_X = m_X^1$ .

If an isotopic substitution is made such that the symmetry of the molecule is lowered, as for example, in the substitution of only one of the Y atoms in  $XY_2$ , then new formulas have to be derived from (III, 1) on the basis of the symmetry of the isotopic molecule. These cases will not be considered here.

### 3. The Sum Rule.

In all cases, except in that of the hydrogen isotope deuterium, the difference in mass  $m^1 - m = \Delta m$  is very small as compared to the mass of the atom. On this basis, simpler formulas can be derived as an approximation for the frequency shifts  $\Delta\omega_j$  of all vibrations  $j$  of the same species  $S$ . For simplification  $R$  will be used in place of the radical in expressions (III, 8), (III, 9), (III, 10) and (III, 11).

Let us consider species  $B_2$  of molecule  $XY_2$  belonging to  $C_{2v}$ . From (III, 8)

$$\omega_3^1 = R \omega_3$$





$$\Delta\omega_3 = \omega_3^1 - \omega_3 = R\omega_3 - \omega_3$$

$$\frac{\Delta\omega_3}{\omega_3} = R - 1 \quad (\text{III, 12})$$

$$R = \left[ \frac{m_Y m_X}{m_Y + \Delta m_Y} \frac{1}{m_X + \Delta m_X} \frac{m_X + \Delta m_X + 2m_Y \sin^2 \alpha + 2\Delta m_Y \sin^2 \alpha}{m_X + 2m_Y \sin^2 \alpha} \right]^{\frac{1}{2}} \quad (\text{III, 13})$$

since

$$m_X^1 = m_X + \Delta m_X,$$

and

$$m_Y^1 = m_Y + \Delta m_Y.$$

Expanding and neglecting quadratic terms in  $\Delta m/m$ , expression (III, 13) reduces to

$$R = \left[ 1 + \frac{-m_X^2 \Delta m_Y - (2m_Y^2 \sin^2 \alpha) \Delta m_X}{(m_X + 2m_Y \sin^2 \alpha)(m_Y + \Delta m_Y)(m_X + \Delta m_X)} \right]^{\frac{1}{2}}. \quad (\text{III, 14})$$

From the binomial expansion and neglecting  $\Delta m/m$  terms of higher order than the first we obtain

$$R = 1 - \frac{1}{2} \frac{m_X^2 \Delta m_Y + (2m_Y^2 \sin^2 \alpha) \Delta m_X}{(m_X + 2m_Y \sin^2 \alpha)(m_Y + \Delta m_Y)(m_X + \Delta m_X)}. \quad (\text{III, 15})$$

Since

$$\frac{\Delta\omega_3}{\omega_3} = R - 1$$



$$\frac{\Delta \omega_3}{\omega_3} = -\frac{1}{2} \frac{m_X^2 \Delta m_Y + (2m_Y^2 \sin^2 \alpha) \Delta m_X}{(m_X + 2m_Y \sin^2 \alpha)(m_Y + \Delta m_Y)(m_X + \Delta m_X)}. \quad (\text{III}, 16)$$

For the end isotope effect  $\Delta m_X = 0$ ; then,

$$\frac{\Delta \omega_3}{\omega_3} = -\frac{1}{2} \frac{m_X \Delta m_Y}{(m_X + 2m_Y \sin^2 \alpha)(m_Y + \Delta m_Y)}. \quad (\text{III}, 17)$$

For the center isotope effect  $m_Y = 0$ ; then,

$$\frac{\Delta \omega_3}{\omega_3} = \frac{-(m_Y \sin^2 \alpha) \Delta m_X}{(m_X + 2m_Y \sin^2 \alpha)(m_X + \Delta m_X)}. \quad (\text{III}, 18)$$

Similarly, an approximate expression will be derived now for the isotope effect in vibrations  $\omega_1$  and  $\omega_2$  of species  $A_1$ .

From (III, 9)

$$\begin{aligned} R &= \frac{\omega_1^1}{\omega_1} \frac{\omega_2^1}{\omega_2} \\ R &= \frac{(\omega_1 + \Delta \omega_1)}{\omega_1} \frac{(\omega_2 + \Delta \omega_2)}{\omega_2} \\ R &= \left(1 + \frac{\Delta \omega_1}{\omega_1}\right) \left(1 + \frac{\Delta \omega_2}{\omega_2}\right). \end{aligned} \quad (\text{III}, 19)$$

Since  $\Delta \omega_1/\omega_1$  and  $\Delta \omega_2/\omega_2$  are very small, the product

$$\frac{\Delta \omega_1}{\omega_1} \frac{\Delta \omega_2}{\omega_2} \rightarrow 0 \text{ and approximately,}$$

$$\frac{\Delta \omega_1}{\omega_1} + \frac{\Delta \omega_2}{\omega_2} = R - 1. \quad (\text{III}, 20)$$





From (III, 9) we may write for R

$$R = \left[ \frac{m_Y^2 m_X}{(m_Y + \Delta m_Y)^2 (m_X + \Delta m_X)} \frac{2(m_Y + \Delta m_Y) + m_X + \Delta m_X}{2m_Y + m_X} \right]^{\frac{1}{2}}. \quad (\text{III}, 21)$$

By expanding and making successive approximations as in the case of the  $B_2$  vibration  $\omega_3$ , we obtain

$$R = 1 - \frac{(m_X m_Y + m_X^2) \Delta m_Y + m_Y^2 \Delta m_X}{(2m_Y + m_X)(m_Y + 2\Delta m_Y)(m_X + \Delta m_X)}. \quad (\text{III}, 22)$$

Therefore,

$$\frac{\Delta \omega_1}{\omega_1} + \frac{\Delta \omega_2}{\omega_2} = - \frac{(m_X m_Y + m_X^2) \Delta m_Y + m_Y^2 \Delta m_X}{(2m_Y + m_X)(m_Y + 2\Delta m_Y)(m_X + \Delta m_X)}. \quad (\text{III}, 23)$$

For the end isotope effect  $\Delta m_X = 0$ ; then

$$\frac{\Delta \omega_1}{\omega_1} + \frac{\Delta \omega_2}{\omega_2} = \frac{-(m_Y + m_X)(\Delta m_Y)}{(2m_Y + m_X)(m_Y + 2\Delta m_Y)}.^* \quad (\text{III}, 24)$$

For the center isotope effect  $\Delta m_Y = 0$ ; then

$$\frac{\Delta \omega_1}{\omega_1} + \frac{\Delta \omega_2}{\omega_2} = \frac{-m_Y \Delta m_X}{(2m_Y + m_X)(m_X + \Delta m_X)}. \quad (\text{III}, 25)$$

Similar approximate relations will be derived below for the

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\* Expressions (III, 17) and (III, 24) have first been derived by E. O. Salant and J. E. Rosenthal<sup>14</sup>.



frequency shifts of the three vibrations of the linear symmetrical  $XY_2$  molecule.

In the case of vibration  $\omega_1$  of species  $\sum_g^+$  (see III, 10):

$$R = \sqrt{\frac{m_Y}{m_Y^1}} = \sqrt{\frac{m_Y}{m_Y + \Delta m_Y}} = \sqrt{1 - \frac{\Delta m_Y}{m_Y + \Delta m_Y}}. \quad (\text{III}, 26)$$

By using the binomial expansion, and neglecting  $\frac{\Delta m_Y}{m_Y + \Delta m_Y}$  terms of higher order than the first we obtain

$$R = 1 - \frac{\Delta m_Y}{2(m_Y + \Delta m_Y)}. \quad (\text{III}, 27)$$

Since  $\Delta\omega_1/\omega_1 = R - 1$ ,

$$\frac{\Delta\omega_1}{\omega_1} = \frac{-\Delta m_Y}{2(m_Y + \Delta m_Y)}. \quad (\text{III}, 28)$$

Expressions (III, 10) and (III, 28) are independent of  $\Delta m_X$ . For the center isotope effect  $\Delta m_Y = 0$  and (III, 28) reduces to  $\Delta\omega_1 = 0$ . This means that the frequency  $\omega_1$  of species  $\sum_g^+$  does not change when only the center atom X is substituted. This is so because the center atom does not take part in this vibration but stays still, and only the end atoms Y move, as shown in Fig. 16. For the end isotope effect relation (III, 28) holds.

Let us consider now the vibrations  $\omega_2$  of species  $\Pi_u$ , and  $\omega_3$  of species  $\sum_u^+$ . From (III, 11) we may write for both vibrations,



$$R = \sqrt{\frac{m_X}{m_X + \Delta m_X} \frac{m_Y}{m_Y + \Delta m_Y} \frac{2(m_Y + \Delta m_Y) + m_X + \Delta m_X}{2m_Y + m_X}}. \quad (\text{III}, 29)$$

By expanding this expression and making successive approximations like in the previous cases

$$R = 1 - \frac{1}{2} \frac{m_X^2 \Delta m_Y + 2m_Y^2 \Delta m_X}{(m_Y + \Delta m_Y)(m_X + \Delta m_X)(m_X + 2m_Y)}. \quad (\text{III}, 30)$$

Therefore,

$$\frac{\Delta \omega_2}{\omega_2} = \frac{\Delta \omega_3}{\omega_3} = - \frac{1}{2} \frac{m_X^2 \Delta m_Y + 2m_Y^2 \Delta m_X}{(m_Y + \Delta m_Y)(m_X + \Delta m_X)(m_X + 2m_Y)}. \quad (\text{III}, 31)$$

For the end isotope effect  $\Delta m_X = 0$ ; then

$$\frac{\Delta \omega_2}{\omega_2} = \frac{\Delta \omega_3}{\omega_3} = \frac{-m_X \Delta m_Y}{2(m_Y + \Delta m_Y)(m_X + 2m_Y)}. \quad (\text{III}, 32)$$

For the center isotope effect  $\Delta m_Y = 0$ ; then

$$\frac{\Delta \omega_2}{\omega_2} = \frac{\Delta \omega_3}{\omega_3} = \frac{-m_Y \Delta m_X}{(m_X + \Delta m_X)(2m_Y + m_X)}. \quad (\text{III}, 33)$$

For all vibrations of the linear molecule, and for the  $B_2$  vibration of the non-linear molecule it can be seen from equations (III, 17), (III, 18), (III, 28), (III, 32) and (III, 33) that in the center isotope effect and in the end isotope effect, the frequency shift  $\Delta \omega$  is negative when  $\Delta m$  is positive, and vice versa. Therefore, the corresponding vibrational bands are shifted to longer wavelength when the substituted isotopic atom is heavier





Table 6.

## Deuterium Substitutions in Bent Symmetrical Triatomic Molecules

Molecule	Observed fundamentals in cm <sup>-1</sup>			Ratios of observed fundamentals		Calculated from product rule		Calculated from product rule		Zero-order frequencies from fundamentals and anharmonicities	Ratios of "observed"
	$\bar{\nu}_1, \bar{\nu}_1^i$	$\bar{\nu}_2, \bar{\nu}_2^i$	$\bar{\nu}_3, \bar{\nu}_3^i$	$\frac{\bar{\nu}_1^i}{\bar{\nu}_1}$	$\frac{\bar{\nu}_2^i}{\bar{\nu}_2}$	$\bar{\nu}_3^i$	$\Delta \bar{\nu}_3$	$\frac{\bar{\omega}_3^i}{\bar{\omega}_3}$	$\frac{\bar{\omega}_1^i \bar{\omega}_2^i}{\bar{\omega}_1 \bar{\omega}_2}$		
H <sub>2</sub> O	3651.7	1595.0	3755.8	0.7425*	0.5390*	2752.6	-1003.2	0.7329*	0.5276*	$\bar{\omega}_1 = 3825.3^*$	$\frac{\bar{\omega}_3^i}{\bar{\omega}_3} = 0.7331$
D <sub>2</sub> O	2666	1178.7	2789							$\bar{\omega}_1 = 2758.1^*$	
										$\bar{\omega}_2 = 1653.9^*$	
										$\bar{\omega}_2 = 1210.3^*$	$\frac{\bar{\omega}_1^i \bar{\omega}_2^i}{\bar{\omega}_1 \bar{\omega}_2} = 0.5275$
										$\bar{\omega}_3 = 3935.6^*$	
										$\bar{\omega}_3 = 2883.7^*$	
H <sub>2</sub> O	3651.7	1595.0	3755.8			2731.6	-1024.2	0.7273	0.5217		
D <sub>2</sub> O <sup>18</sup>											
H <sub>2</sub> S	2610.8	1290	2684	0.7448*	0.5246*	1928.1	-756	0.7184*	0.5150*		
D <sub>2</sub> S	1891.6	934	1999								



Table 6 (continued)

## Deuterium Substitutions in Bent Symmetrical Triatomic Molecules

Molecule	Observed fundamentals in cm <sup>-1</sup>			Ratios of observed fundamentals		Calculated from product rule		Calculated from product rule		Zero-order frequencies from fundamentals and anharmonicities	Ratios of "observed"
	$\bar{\nu}_1, \bar{\nu}_1^i$	$\bar{\nu}_2, \bar{\nu}_2^i$	$\bar{\nu}_3, \bar{\nu}_3^i$	$\frac{\bar{\nu}_3^i}{\bar{\nu}_3}$	$\frac{\bar{\nu}_1^i \bar{\nu}_2^i}{\bar{\nu}_1 \bar{\nu}_2}$	$\frac{\bar{\nu}_3^i}{\bar{\nu}_3}$	$\Delta \bar{\nu}_3$	$\frac{\bar{\omega}_3^i}{\bar{\omega}_3}$	$\frac{\bar{\omega}_1^i \bar{\omega}_2^i}{\bar{\omega}_1 \bar{\omega}_2}$		
H <sub>2</sub> S D <sub>2</sub> S <sup>34</sup>	2610.8	1290	2684			1925.0	- 759	0.7172	0.5133		
H <sub>2</sub> Se D <sub>2</sub> Se (ref.15)	2260 1630	1074 745	2350 1696	0.7217*	0.5003*	1672.7	- 677.3	0.7118*	0.5066*		
H <sub>2</sub> Se D <sub>2</sub> Se <sup>78</sup> (ref.15)	2260	1074	2350			1673.2	- 676.8	0.7120	0.5068		
CH <sub>2</sub> CD <sub>2</sub> (ref.16)	2968	1444	3000			2232.3	- 767.7	0.7441	0.5351		





Table 6 (continued)

## Deuterium Substitutions in Bent Symmetrical Triatomic Molecules

Molecule	Observed fundamentals in cm <sup>-1</sup>			Ratios of observed fundamentals		Calculated from product rule		Calculated from product rule		Zero-order frequencies from fundamentals and anharmonicities	Ratios of "observed"
	$\bar{\nu}_1, \bar{\nu}_1^i$	$\bar{\nu}_2, \bar{\nu}_2^i$	$\bar{\nu}_3, \bar{\nu}_3^i$	$\frac{\bar{\nu}_1^i}{\bar{\nu}_3}$	$\frac{\bar{\nu}_1^i \bar{\nu}_2^i}{\bar{\nu}_1 \bar{\nu}_2}$	$\bar{\nu}_3^i$	$\Delta \bar{\nu}_3$	$\frac{\bar{\omega}_3^i}{\bar{\omega}_3}$	$\frac{\bar{\omega}_1^i \bar{\omega}_2^i}{\bar{\omega}_1 \bar{\omega}_2}$		
CH <sub>2</sub> C <sup>13</sup> D <sub>2</sub> (ref.16)	2968	1444	3000			2217.2	- 782.8	0.7391	0.5299		

\* These values have been taken from G. Herzberg's book.<sup>1</sup>



Table 7.

## Bent Symmetrical Triatomic Molecules

Molecular Pair	Observed fundamentals of ordinary molecule in $\text{cm}^{-1}$			Calculated from sum rule		Calculated from sum rule		Zero-order frequency $\bar{\omega}_3$ from fundamental $\bar{\nu}_3$ and anharmonicities	Calculated from sum rule $\bar{\omega}_3^i$ $\Delta \bar{\omega}_3$
	$\bar{\nu}_1$	$\bar{\nu}_2$	$\bar{\nu}_3$	$\Delta \bar{\nu}_3$	$\bar{\nu}_3^i$	$\frac{\Delta \bar{\omega}_3}{\bar{\omega}_3}$	$\frac{\Delta \bar{\omega}_1}{\bar{\omega}_1} + \frac{\Delta \bar{\omega}_2}{\bar{\omega}_2}$		
$\text{H}_2\text{O}-\text{H}_2\text{O}^{18}$	3651.7	1595.0	3755.8	-4.9	3750.9	-0.00130	-0.00623	3935.6	3930.5 - 5.1
$\text{H}_2\text{S}-\text{H}_2\text{S}^{34}$	2610.8	1290	2684	-2.5	2681.5	-0.00093	-0.00174		
$\text{H}_2\text{Se}-\text{H}_2\text{Se}^{78}$ (ref. 15)	2260	1074	2350	+0.4	2350.4	+0.00016	+0.00032		
$\text{SO}_2-\text{SO}_2^{18}$	1151.2	519	1361	-42.5	1318.5	-0.03126	-0.07510		
$\text{SO}_2-\text{S}^{34}\text{O}_2$	1151.2	519	1361	-17.5	1343.5	-0.01287	-0.01469		
$\text{SO}_2-\text{S}^{34}\text{O}_2^{18}$	1151.2	519	1361	-55.6	1305.4	-0.04086	-0.08085		
$\text{ClO}_2-\text{ClO}_2^{18}$ (ref. 17 & 18)	946	527	1109	-34.4	1074.6	-0.03105	-0.07623		
$\text{ClO}_2-\text{Cl}^{37}\text{O}_2$ (ref. 17 & 18)	946	527	1109	-13.2	1095.8	-0.01194	-0.01290		



Table 7 (continued). Bent Symmetrical Triatomic Molecules

Molecular Pair	Observed fundamentals of ordinary molecule in $\text{cm}^{-1}$			Calculated from sum rule		Calculated from sum rule		Zero-order frequency $\omega_3$ from fundamental $\bar{\nu}_3$ and anharmonicities	Calculated from sum rule $-\frac{1}{\omega_3^2} \Delta \bar{\omega}_3$
	$\bar{\nu}_1$	$\bar{\nu}_2$	$\bar{\nu}_3$	$\Delta \bar{\nu}_3$	$\frac{\bar{\nu}_3^2}{\bar{\nu}_3}$	$\frac{\Delta \bar{\omega}_3}{\bar{\omega}_3}$	$\frac{4\bar{\omega}_1}{\bar{\omega}_1} + \frac{\Delta \bar{\omega}_2}{\bar{\omega}_2}$		
$\text{ClO}_2\text{-Cl}^{37}\text{O}_2^{18}$ (ref. 17 & 18)	946	527	1109	-44.3	1064.7	-0.03999	-0.08243		
$\text{NO}_2\text{-NO}_2^{18}$	1320	648	1621	-40.7	1580.3	-0.0251	-0.06532		
$\text{NO}_2\text{-N}^{15}\text{O}_2$	1320	648	1621	-34.0	1587.0	-0.02099	-0.02312		
$\text{NO}_2\text{-N}^{15}\text{O}_2^{18}$	1320	648	1621	-61.3	1559.7	-0.0378	-0.07946		
$\text{Cl}_2\text{O-Cl}_2\text{O}^{18}$ (ref. 19)	680	330	973	-41.0	932.0	-0.04211	-0.04529		
$\text{Cl}_2\text{O-Cl}_2\text{O}^{37}$ (ref. 19)	680	330	973	-6.4	966.6	-0.0066	-0.03040		
$\text{Cl}_2\text{O-Cl}_2\text{O}^{37}\text{O}^{18}$ (ref. 19)	680	330	973	-44.5	928.6	-0.0457	-0.06766		
$\text{CH}_2\text{-C}^{13}\text{H}_2$ (ref. 16)	2968	1444	3000	-12.4	2987.6	-0.00412	-0.00555		
$\text{F}_2\text{-F}_2\text{O}^{18}$ (ref. 20)	830	490	1110	-36.0	1074.0	-0.0324	-0.0392		





Table 8.

## Linear Symmetrical Triatomic Molecules

	$\text{CO}_2\text{-CO}_2^{18}$	$\text{CO}_2\text{-C}^{13}\text{O}_2$	$\text{CO}_2\text{-C}^{13}\text{O}_2^{18}$	$\text{CS}_2\text{-CS}_2^{34}$	$\text{CS}_2\text{-C}^{13}\text{S}_2$	$\text{CS}_2\text{-C}^{13}\text{S}_2^{34}$
$\bar{\nu}_1$	1388.3	1388.3	1388.3	656.5	656.5	656.5
$\bar{\nu}_2$	667.3	667.3	667.3	396.7	396.7	396.7
$\bar{\nu}_3$	2349.3	2349.3	2349.3	1523	1523	1523
$\bar{\nu}_1^i$	1311.1	1388.3	1311.1	637.2	656.5	637.2
$\bar{\nu}_2^i$	657.2	648.6	641.32	394.9	383.8	382.87
$\bar{\nu}_3^i$	2313.64	2283.4	2257.82	1515.9	1473.5	1469.91
Observed (cm <sup>-1</sup> ) (ref. 21)	2283.6					
$\bar{\omega}_1$	1351.2	1351.2	1351.2			
$\bar{\omega}_2$	672.2	672.2	672.2			
$\bar{\omega}_3$	2396.4	2396.4	2396.4			
Zero-order frequencies from fundamentals and anharmonicities (cm <sup>-1</sup> )						



Table 8 (continued). Linear Symmetrical Triatomic Molecules

	$\text{CO}_2\text{-CO}_2^{18}$	$\text{CO}_2\text{-C}^{13}\text{O}_2$	$\text{CO}_2\text{-C}^{13}\text{O}_2^{18}$	$\text{CS}_2\text{-CS}_2^{34}$	$\text{CS}_2\text{-C}^{13}\text{S}_2$	$\text{CS}_2\text{-C}^{13}\text{S}_2^{34}$
$\bar{\omega}_1$	1276.0	1351.2	1276.0			
Calculated from sum rule ( $\text{cm}^{-1}$ )	662.0	653.3	646.0			
$\bar{\omega}_2$	2360.0	2329.2	2303.1			
$\bar{\omega}_3$	- 77.3	0	- 77.3	- 19.3	0	- 19.3
$\Delta \bar{\nu}_1$	- 10.1	- 18.7	- 26.0	- 1.8	- 12.9	- 13.8
Calculated from sum rule ( $\text{cm}^{-1}$ )	- 35.7	- 65.9	- 91.5	- 7.1	- 49.5	- 53.1
$\Delta \bar{\nu}_2$	- 75.2	0	- 75.2			
$\Delta \bar{\nu}_3$	- 10.2	- 18.9	- 26.2			
Calculated from sum rule ( $\text{cm}^{-1}$ )	- 36.4	- 67.2	- 93.3			
$\Delta \bar{\omega}_1$	- 0.05565	0	- 0.05565	- 0.02937	0	- 0.02937
$\Delta \bar{\omega}_2$	- 0.01518	- 0.02806	- 0.03894	- 0.00464	- 0.03248	- 0.03486
$\Delta \bar{\omega}_3$						
Calculated from sum rule ( $\text{cm}^{-1}$ )						
$\frac{\Delta \bar{\omega}_1}{\bar{\omega}_1}$						
$\frac{\Delta \bar{\omega}_2}{\bar{\omega}_2} = \frac{\Delta \bar{\omega}_3}{\bar{\omega}_3}$						





than the ordinary atom. Similarly, they are shifted to shorter wavelength when the isotope is lighter than the ordinary atom. In the case of the two  $A_1$  vibrations in the non-linear molecule, nothing can be said in this respect for each vibration separately; but equations (III, 24) and (III, 25) show that

$$\frac{\Delta \omega_1}{\omega_1} + \frac{\Delta \omega_2}{\omega_2} \lesseqgtr 0$$

according to whether  $\Delta m_Y \gtrless 0$  respectively.

In general, for all vibrations  $f$  of any species  $S$ , an approximate expression can be derived which gives the value of the sum  $\frac{\Delta \omega_1}{\omega_1} + \frac{\Delta \omega_2}{\omega_2} + \frac{\Delta \omega_3}{\omega_3} + \dots + \frac{\Delta \omega_f}{\omega_f}$  in terms of the masses of the atoms and the geometrical structure of the molecule. The expression is called the sum rule because it gives the value of the sum  $\sum_{j=1}^f \frac{\Delta \omega_j}{\omega_j}$ . It is an approximation of the product rule. Expressions (III, 16), (III, 23), (III, 28) and (III, 31) are special cases of the sum rule, and they hold only when  $\Delta m$  is small as compared to  $m$ . Therefore, in the case of deuterium substitutions for hydrogen atoms, the exact formulas (III, 8), (III, 9), (III, 10) and (III, 11) should be used.

The expressions derived in this chapter regarding the isotope effect have been applied to some triatomic molecules  $XY_2$ . The results are collected in Tables 6, 7 and 8.

#### 4. Discussion of the tables.

Unless otherwise stated the observed frequencies in Tables 6, 7 and 8, and also in the following pages, have been taken from



Herzberg's book<sup>1</sup>. In these three tables the most abundant atom is always considered the ordinary atom and the substituted isotope is the atom second in abundance. The masses of the atoms and their isotopes are those given by Livingston and Bethe<sup>22</sup>.

Table 6 refers to deuterium substitutions for hydrogen atoms in bent  $XY_2$  molecules of point group  $C_{2v}$ . Since in this case  $\Delta m/m$  is of the order of 1 the strict product rule has been used for the calculations. The fact that the product rule holds better for the zero-order frequencies  $\bar{\omega}$  than for the fundamentals  $\bar{\nu}$  is demonstrated by the example of  $H_2O - D_2O$ .

Table 7 includes isotopic substitutions different from those of the hydrogen isotope deuterium in  $XY_2$  molecules of the same point group  $C_{2v}$ . Since  $\Delta m/m$  is very small in this case, the sum rule has been used in the calculations. By comparing column 3 of Table 7 and column 3 of Table 6 it can be seen how much larger the frequency shift  $\Delta \bar{\nu}_3$  is, resulting from deuterium substitutions than the corresponding shift from other isotopic substitutions. The quantities  $\Delta \bar{\omega}_3 / \bar{\omega}_3$  and  $\frac{\Delta \bar{\omega}_1}{\bar{\omega}_1} + \frac{\Delta \bar{\omega}_2}{\bar{\omega}_2}$  in Table 7 are all negative, except for the pair  $H_2Se - H_2Se^{78}$ , since this is the only case in which the substituted isotope is lighter than the ordinary atom.

In Table 8, which refers to linear  $XY_2$  molecules of point group  $D_{\infty h}$ , the calculations have been done by also using the sum rule, for the reason already mentioned. The second row of this table contains the calculated values of the three frequencies  $\bar{\nu}_1^1$ ,  $\bar{\nu}_2^1$ ,  $\bar{\nu}_3^1$  of the isotopic molecule. It may be seen that, if





a complete substitution of all three atoms is carried out in the linear molecules of Table 8 or in the bent molecules of Table 7, the quantities  $\Delta\bar{\omega}_j/\bar{\omega}_j$  and  $\frac{\Delta\bar{\omega}_1}{\bar{\omega}_1} + \frac{\Delta\bar{\omega}_2}{\bar{\omega}_2}$  become almost equal to the sum of the corresponding quantities if the center and end isotope effects are considered separately. For example in the case of  $\text{SO}_2$ , for the end isotope effect  $\Delta\bar{\omega}_3/\bar{\omega}_3 = -0.03126$ , for the center isotope effect  $\Delta\bar{\omega}_3/\bar{\omega}_3 = -0.01287$ , and when the three atoms are substituted  $\Delta\bar{\omega}_3/\bar{\omega}_3 = -0.04086$ .

One interesting fact in Table 7 is that the only case in which the frequency shifts are larger for the center isotope effect than for the end isotope effect is that of the  $\text{Cl}_2\text{O}$  molecule. Even though two atoms are substituted in the end isotope effect while only one atom oxygen is substituted in the center isotope effect, still in this case the shift is larger for the center atom substitution than for the substitution of the end atoms of chlorine. The reason is that, because of the large mass of chlorine, these atoms vibrate with a very small amplitude while the center atom oxygen, which is much lighter, has a larger amplitude of vibration.

It was mentioned earlier in this thesis that the knowledge of the frequencies of isotopic molecules is very important in the determination of the field of force of molecules. In addition, the investigation of the frequency shifts upon isotopic substitutions is helpful in correlating the observed vibrational frequencies with the theoretical normal modes of vibration. For example, in  $\text{CH}_3\text{Cl}$  there is only one fundamental frequency  $732\text{ cm}^{-1}$  which shows an appreciable shift when  $\text{Cl}^{35}$  is substituted by  $\text{Cl}^{37}$ .





Therefore it must correspond to the C - Cl vibration.

Another very interesting possibility of application of the isotope effect has just been published. Bigeleisen and Goeppert Mayer<sup>23</sup> have worked out tables and approximation methods from which a rapid calculation of equilibrium constants is possible if the frequency shifts on isotopic substitution are known.

### 5. The Noether Ratio Rule.

An empirical relation for calculating the frequencies of isotopic groups in some molecules has been proposed by Noether<sup>24</sup>. The relation was found in an investigation of the isotopic methyl halides and it states that

$$\left( \frac{\nu_k^1}{\nu_k} \right)_{\text{CH}_3\text{X}'} = \left( \frac{\nu_k^1}{\nu_k} \right)_{\text{CH}_3\text{X}''} \quad (\text{III}, 34)$$

where  $\nu_k^1$  refers to the frequency of the k-th vibration of the heavy molecule  $\text{CD}_3\text{X}$ . No theoretical derivation of this rule has been given. Experimental data shows that it holds rather well for the methyl halides  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_3\text{Br}$  but not as well for other cases like  $\text{CH}_3\text{OH}$ ,  $\text{CH}_3\text{OD}$ ,  $\text{CH}_3\text{NO}_2$ . Also, Noether's data show that the rule works better for some vibrations than for others, in the same pairs of molecules. The rule was applied also to the series  $\text{H}_2\text{O} - \text{D}_2\text{O}$ ,  $\text{H}_2\text{S} - \text{D}_2\text{S}$ ,  $\text{H}_2\text{Se} - \text{D}_2\text{Se}$ , but here the agreement between calculated and observed frequencies is poorer than in the before mentioned cases.

We may examine the connection between the Noether rule and the Redlich-Teller product rule, and we choose, as examples, the

most common to the 2 - 11 vibration.

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### Ratio Rule.

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is found in some cases. It is expressed as follows:

was found in an examination of the isotopic ratios

it is stated that

$$\frac{\nu_1}{\nu_2} = \frac{\sqrt{\frac{m_2}{m_1}}}{\sqrt{\frac{m_2}{m_1}}}$$

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of the 2-11 vibration. The theoretical

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of molecules. The rule was applied to the

15 - 16, 17 - 18, 19 - 20, but none the agreement between

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methyl halides  $\text{CH}_3\text{Cl} - \text{CD}_3\text{Cl}$  and  $\text{CH}_3\text{Br} - \text{CD}_3\text{Br}$ . These molecules belong to the point group  $\text{C}_{3v}$  and have three vibrations  $\nu_1, \nu_2$  and  $\nu_3$  of species  $A_1$  and three doubly degenerate vibrations  $\nu_4, \nu_5$ , and  $\nu_6$  of species E. The product rule may be used for our present purpose for the fundamentals instead of the zero-order frequencies. In doing so the product rule for the  $A_1$  vibrations in  $\text{CH}_3\text{Cl} - \text{CD}_3\text{Cl}$  takes the form:

$$\left( \frac{\nu_1^1 \nu_2^1 \nu_3^1}{\nu_1 \nu_2 \nu_3} \right)_{\text{CH}_3\text{Cl}} = \frac{m_H}{m_D} \sqrt{\frac{m_{\text{Cl}} + m_C + 3m_D}{m_{\text{Cl}} + m_C + 3m_H}} \quad (\text{III}, 35)$$

Similarly for  $\text{CH}_3\text{Br} - \text{CD}_3\text{Br}$

$$\left( \frac{\nu_1^1 \nu_2^1 \nu_3^1}{\nu_1 \nu_2 \nu_3} \right)_{\text{CH}_3\text{Br}} = \frac{m_H}{m_D} \sqrt{\frac{m_{\text{Br}} + m_C + 3m_D}{m_{\text{Br}} + m_C + 3m_H}} \quad (\text{III}, 36)$$

Giving the values 1, 2, and 3, successively, to  $k$  in (III, 34) and multiplying the resulting three equations, the Noether rule demands that

$$\left( \frac{\nu_1^1 \nu_2^1 \nu_3^1}{\nu_1 \nu_2 \nu_3} \right)_{\text{CH}_3\text{Cl}} = \left( \frac{\nu_1^1 \nu_2^1 \nu_3^1}{\nu_1 \nu_2 \nu_3} \right)_{\text{CH}_3\text{Br}} \quad (\text{III}, 37)$$

From (III, 35) and (III, 36) it can be seen that the last equation holds strictly only if  $m_D = m_H$  or  $m_{\text{Cl}} = m_{\text{Br}}$ , which, of course, is not the case. A similar procedure can be followed with vibrations  $\nu_4, \nu_5$  and  $\nu_6$  leading to the same result. Therefore the Noether rule has no strict validity.

However, it may be understood why the experimental data



support the rule so well for some vibrations and approximately, although not as well, for other vibrations in these molecules. The reason is that the halogens are very heavy in comparison with the other light atoms so that the masses of Cl and Br may be considered as almost equal in this approximation. The right-hand side of expressions (III, 35) and (III, 36) reduces then to a constant if  $m_H$  and  $m_D$  are neglected under the square root:

$$\frac{\nu_1^1 \nu_2^1 \nu_3^1}{\nu_1 \nu_2 \nu_3} = \frac{m_H}{m_D} = \text{constant.} \quad (\text{III, 38})$$

The validity of this relation was tested by putting in it the experimental frequency values of the two methyl halides. The following table gives the results:

Table 9.

	$\bar{\nu}_1$ (cm <sup>-1</sup> )	$\bar{\nu}_2$ (cm <sup>-1</sup> )	$\bar{\nu}_3$ (cm <sup>-1</sup> )	$\frac{(\nu_1 \nu_2 \nu_3)_{CD_3X}}{(\nu_1 \nu_2 \nu_3)_{CH_3X}}$	$\frac{m_H}{m_D}$
CH <sub>3</sub> Cl	2966.2	1354.9	732.1	0.526	0.500
CD <sub>3</sub> Cl	2161	1029	695		
CH <sub>3</sub> Br	2972	1305.1	611	0.517	0.500
CD <sub>3</sub> Br	2151	987	577		

As may be expected, relation (III, 38) is better fulfilled for the heavier of the two halides.

For vibrations  $\nu_4$ ,  $\nu_5$  and  $\nu_6$  of species E the product





rule takes the form:

$$\left( \frac{\nu_4^1 \nu_5^1 \nu_6^1}{\nu_4 \nu_5 \nu_6} \right)_{\text{CH}_3\text{Cl}} = \sqrt{\frac{m_H^3 (m_{\text{Cl}} + m_{\text{C}} + 3m_{\text{D}}) \frac{I_1^1}{I}}{m_D^3 (m_{\text{Cl}} + m_{\text{C}} + 3m_{\text{H}}) \frac{I}{I_1}}}. \quad (\text{III}, 39)$$

Here  $I$  and  $I_1^1$  are the moments of inertia of the molecules  $\text{CH}_3\text{Cl}$  and  $\text{CD}_3\text{Cl}$  respectively, about an axis perpendicular to the symmetry axis.

Similarly, for  $\text{CH}_3\text{Br}$  and  $\text{CD}_3\text{Br}$ ,

$$\left( \frac{\nu_4^1 \nu_5^1 \nu_6^1}{\nu_4 \nu_5 \nu_6} \right)_{\text{CH}_3\text{Br}} = \sqrt{\frac{m_H^3 (m_{\text{Br}} + m_{\text{C}} + 3m_{\text{D}}) \frac{I_1^1}{I_1}}{m_D^3 (m_{\text{Br}} + m_{\text{C}} + 3m_{\text{H}}) \frac{I_1}{I_1}}}. \quad (\text{III}, 40)$$

For the same reasons as outlined before, (III, 39) and (III, 40) may be reduced to the approximately correct relation

$$\begin{aligned} \left( \frac{\nu_4^1 \nu_5^1 \nu_6^1}{\nu_4 \nu_5 \nu_6} \right)_{\text{CH}_3\text{Cl}} &= \left( \frac{\nu_4^1 \nu_5^1 \nu_6^1}{\nu_4 \nu_5 \nu_6} \right)_{\text{CH}_3\text{Br}} \\ &= \sqrt{\frac{m_H^3}{m_D^3}} = \text{constant}. \end{aligned} \quad (\text{III}, 41)$$

Here the approximation is stretched a little further since the two moments of inertia have also been taken as equal. This may explain in part why the experimental agreement in this case is not as good as in the case of vibrations  $\nu_1$ ,  $\nu_2$  and  $\nu_3$ , as may be seen by comparing Tables 9 and 10.



Table 10.

	$\bar{\nu}_4$ (cm <sup>-1</sup> )	$\bar{\nu}_5$ (cm <sup>-1</sup> )	$\bar{\nu}_6$ (cm <sup>-1</sup> )	$\frac{(\nu_4 \nu_5 \nu_6)_{\text{CD}_3\text{X}}}{(\nu_4 \nu_5 \nu_6)_{\text{CH}_3\text{X}}}$	$\frac{\bar{m}_\text{H}^3}{\bar{m}_\text{D}^3}$
CH <sub>3</sub> Cl	3041.8	1454.6	1015.0		
CD <sub>3</sub> Cl	2286	1058	775	0.417	0.354
CH <sub>3</sub> Br	3055.9	1445.3	952.0		
CD <sub>3</sub> Br	2293	1053	717	0.412	0.354

Although the products  $\frac{\nu_1^1 \nu_2^1 \nu_3^1}{\nu_1 \nu_2 \nu_3}$  and  $\frac{\nu_4^1 \nu_5^1 \nu_6^1}{\nu_4 \nu_5 \nu_6}$  are independ-

ent of the force constants, the splitted quantities  $\nu_1^1/\nu_1$ ,  $\nu_2^1/\nu_2$ ,  $\nu_3^1/\nu_3$  and  $\nu_4^1/\nu_4$ ,  $\nu_5^1/\nu_5$ ,  $\nu_6^1/\nu_6$  are functions of the force constants. The force constants are, with the exception of the  $k$  for the C-halogen bond, very similar for both methyl halides<sup>25,16</sup>. Since furthermore the dependence of the products on the masses  $m_{\text{Cl}}$  and  $m_{\text{Br}}$  may be considered to be approximately the same, the separated ratios  $\nu_1^1/\nu_1$ ,  $\nu_2^1/\nu_2$ , ... may also be approximately constant. With these restrictions in mind the Noether rule can be justified. It should hold better for the heavier methyl halides, and it should be particularly applicable to vibrations in which the hydrogens are mainly participating, while the heavy halogens are practically standing still. This condition applies to vibrations  $\nu_1$ ,  $\nu_2$ ,  $\nu_4$  and  $\nu_5$  and it may be seen from Table 15 that the ratio rule is well confirmed in these cases. In the case of vibration  $\nu_6$  which is the bending





vibration of the whole molecule, the rule does not hold so well, as may be expected. On the other hand, in the case of vibration  $\nu_3$ , which is the halogen-carbon valence vibration, the rule is seen to hold as well as for the  $\text{CH}_3$  vibrations. This may be easily understood since the hydrogens partake very little in this vibration. Hence, when the deuterium atoms are substituted, the shift is practically zero for both methyl halides and the ratio  $\nu_3^1/\nu_3$  is very nearly 1 in both cases.

Noether's ratio rule should hold approximately also for other molecules that satisfy the same or similar conditions as the discussed methyl halides, i.e., that they contain hydrogen and some very heavy atom or atoms. Let us consider as an example chloroform ( $\text{CHCl}_3$ ), bromoform ( $\text{CHBr}_3$ ), and the corresponding "heavy" molecules  $\text{CDCl}_3$  and  $\text{CDBr}_3$ . The results obtained by applying the rule to these molecules are tabulated below.\*

Table 11.

k	$\text{CHBr}_3\text{-CDBr}_3$			$\text{CHCl}_3\text{-CDCl}_3$		
	$\bar{\nu}_k$ obs.	$\bar{\nu}_k^1$ obs.	$\nu_k^1/\nu_k$ obs.	$\bar{\nu}_k$ obs.	$\bar{\nu}_k^1$ obs.	$\nu_k^1/\nu_k$ obs.
1	3023	2247	0.743	3018.9	2256.0	0.747
2	538.6	519.3	0.964	668.3	650.8	0.974
3	222.3	221.6	0.997	365.9	366.5	1.0016
4	1142	840	0.736	1215.6	908.3	0.747
5	656	628.5	0.958	761.2	737.6	0.969
6	153.8	153.8	0.997	262.0	262.0	1.00

\* The frequencies used are those observed in the liquid. Those of  $\text{CHBr}_3$  and  $\text{CDBr}_3$  are given by O. Redlich and W. Stricks<sup>26</sup>.



In the case of the vibrations  $\nu_3$  and  $\nu_6$  the shift is practically zero, which means that the hydrogen atom has very little part in these vibrations. Therefore, fulfillment of the ratio rule in these cases is trivial. The vibrations  $\nu_1$  and  $\nu_4$  show the largest shift. Of these, the rule gives the best agreement for  $\nu_1$  which is a hydrogen vibration. For the remaining frequencies the results are about the same, but relatively, the agreement is better for  $\nu_4$  since in this vibration the shift is much greater than in the others. The general conclusions are the same as were discussed for the methyl halides.

Applying the product rule to the two species of vibrations  $A_1$  and E characteristic of group  $C_{3v}$ , leads to the expressions:

$$\left( \frac{\nu_1^1 \nu_2^1 \nu_3^1}{\nu_1 \nu_2 \nu_3} \right)_{\text{CHBr}_3} = \sqrt{\frac{m_H}{m_D} \frac{(m_C + 3m_{\text{Br}} + m_D)}{(m_C + 3m_{\text{Br}} + m_H)}}, \quad (\text{III}, 42)$$

$$\left( \frac{\nu_1^1 \nu_2^1 \nu_3^1}{\nu_1 \nu_2 \nu_3} \right)_{\text{CHCl}_3} = \sqrt{\frac{m_H}{m_D} \frac{(m_C + 3m_{\text{Cl}} + m_D)}{(m_C + 3m_{\text{Cl}} + m_H)}},$$

and

$$\left( \frac{\nu_4^1 \nu_5^1 \nu_6^1}{\nu_4 \nu_5 \nu_6} \right)_{\text{CHBr}_3} = \sqrt{\frac{m_H}{m_D} \frac{(m_C + 3m_{\text{Br}} + m_D)}{(m_C + 3m_{\text{Br}} + m_H)} \frac{I_1^1}{I_1}}, \quad (\text{III}, 43)$$

$$\left( \frac{\nu_4^1 \nu_5^1 \nu_6^1}{\nu_4 \nu_5 \nu_6} \right)_{\text{CHCl}_3} = \sqrt{\frac{m_H}{m_D} \frac{(m_C + 3m_{\text{Cl}} + m_D)}{(m_C + 3m_{\text{Cl}} + m_H)} \frac{I_1^1}{I_1}}.$$

They may be reduced to simpler expressions in the manner employed



for the methyl halides. For chloroform and bromoform and their isotopic molecules we obtain

$$\begin{aligned}
 \left( \frac{\nu_1^1 \nu_2^1 \nu_3^1}{\nu_1 \nu_2 \nu_3} \right)_{\text{CHCl}_3} &= \left( \frac{\nu_1^1 \nu_2^1 \nu_3^1}{\nu_1 \nu_2 \nu_3} \right)_{\text{CHBr}_3} = \left( \frac{\nu_4^1 \nu_5^1 \nu_6^1}{\nu_4 \nu_5 \nu_6} \right)_{\text{CHCl}_3} \\
 &= \left( \frac{\nu_4^1 \nu_5^1 \nu_6^1}{\nu_4 \nu_5 \nu_6} \right)_{\text{CHBr}_3} = \sqrt{\frac{m_H}{m_D}}. \quad (\text{III, 44})
 \end{aligned}$$

Table 12 shows the validity of the simplified relation (III, 44). It must be considered as good.

Table 12.

	$\frac{\nu_1^1 \nu_2^1 \nu_3^1}{\nu_1 \nu_2 \nu_3}$ (obs.)	$\frac{\nu_4^1 \nu_5^1 \nu_6^1}{\nu_4 \nu_5 \nu_6}$ (obs.)	$\sqrt{\frac{m_H}{m_D}}$
$\text{CHCl}_3\text{-CDCl}_3$	0.729	0.716	0.707
$\text{CHBr}_3\text{-CDBr}_3$	0.714	0.703	0.707

Comparison of this table with Tables 9 and 10 shows what we expect: namely, a better agreement for chloroform and bromoform than for the methyl halides because of the presence of the three heavy halogens instead of one.

In the case of the series  $\text{H}_2\text{O} - \text{D}_2\text{O}$ ,  $\text{H}_2\text{S} - \text{D}_2\text{S}$ ,  $\text{H}_2\text{Se} - \text{D}_2\text{Se}$ , the ratio rule is expected to hold better for the molecules  $\text{H}_2\text{S} - \text{D}_2\text{S}$  and  $\text{H}_2\text{Se} - \text{D}_2\text{Se}$  than for the case of  $\text{H}_2\text{O} - \text{D}_2\text{O}$ , since S and Se are much heavier than O.





The results of applying the rule to these molecules are shown in Table 13.

Table 13.

k	H <sub>2</sub> O-D <sub>2</sub> O	H <sub>2</sub> S-D <sub>2</sub> S	H <sub>2</sub> Se-D <sub>2</sub> Se
	$\frac{\nu_k}{\nu_k}$	$\frac{\nu_k}{\nu_k}$	$\frac{\nu_k}{\nu_k}$
	obs.	obs.	obs.
1	0.7301	0.7245	0.7212
2	0.7390	0.7240	0.6937
3	0.7425	0.7449	0.7217

It is seen that the rule holds better for the symmetrical vibrations  $\nu_1$  and  $\nu_2$  which are mainly hydrogen vibrations.

In analogy to the procedure applied to molecules of group  $C_{3v}$  (methyl halides, etc.) we may deduce a simplified product rule also for the mentioned triatomic molecules of symmetry  $C_{2v}$ :

$$\frac{\nu_3^1}{\nu_3}_{H_2O} = \frac{\nu_3^1}{\nu_3}_{H_2S} = \frac{\nu_3^1}{\nu_3}_{H_2Se} = \sqrt{\frac{m_H}{m_D}} \quad (\text{III}, 45)$$

and

$$\frac{\nu_1^1 \nu_2^1}{\nu_1 \nu_2}_{H_2O} = \frac{\nu_1^1 \nu_2^1}{\nu_1 \nu_2}_{H_2S} = \frac{\nu_1^1 \nu_2^1}{\nu_1 \nu_2}_{H_2Se} = \frac{m_H}{m_D}. \quad (\text{III}, 46)$$

Table 14 shows that these relations hold more or less approximately.



Table 14.

Molecular Pair	$\frac{\nu_3^1}{\nu_3}$	$\sqrt{\frac{m_H}{m_D}}$	$\frac{\nu_1^1 \nu_2^1}{\nu_1 \nu_2}$	$\frac{m_H}{m_D}$
	obs.		obs.	
H <sub>2</sub> O-D <sub>2</sub> O	0.7425	0.707	0.5390	0.500
H <sub>2</sub> S-D <sub>2</sub> S	0.7449	0.707	0.5246	0.500
H <sub>2</sub> Se-D <sub>2</sub> Se	0.7217	0.707	0.5003	0.500

As expected the best agreement is obtained for the pair H<sub>2</sub>Se-D<sub>2</sub>Se and the next best for H<sub>2</sub>S - D<sub>2</sub>S, with the exception of the observed  $\nu_3^1/\nu_3$  for H<sub>2</sub>Se - D<sub>2</sub>Se. But this discrepancy may be due to an experimental error in the determination of the band centers, as Herzberg<sup>1</sup> pointed out.

As a last example the molecular pairs CH<sub>3</sub>OH - CD<sub>3</sub>OH, CH<sub>3</sub>OD - CD<sub>3</sub>OD and CH<sub>3</sub>NO<sub>2</sub> - CD<sub>3</sub>NO<sub>2</sub> may be compared with the pairs CH<sub>3</sub>Br - CD<sub>3</sub>Br and CH<sub>3</sub>Cl - CD<sub>3</sub>Cl. The frequency values for the first three pairs have been taken from reference 15.

Table 15.

	CH <sub>3</sub> Br-CD <sub>3</sub> Br $\frac{\nu_k^i}{\nu_k}$ obs.	CH <sub>3</sub> Cl-CD <sub>3</sub> Cl $\frac{\nu_k^i}{\nu_k}$ obs.	CH <sub>3</sub> OH-CD <sub>3</sub> OH $\frac{\nu_k^i}{\nu_k}$ obs.	CH <sub>3</sub> OD-CD <sub>3</sub> OD $\frac{\nu_k^i}{\nu_k}$ obs.	CH <sub>3</sub> NO <sub>2</sub> -CD <sub>3</sub> NO <sub>2</sub> $\frac{\nu_k^i}{\nu_k}$ obs.
1	0.7238	0.7285	0.7360	0.7302	0.7403
2	0.7563	0.7595	0.7718	0.7683	0.7714
3	0.9444	0.9493	0.9574	0.9490	0.9544
4	0.7504	0.7515	0.7495	0.7511	0.7513
5	0.7286	0.7273	0.7312	(0.7264) (0.7323)	0.7258
6	0.7532	0.7635	0.6968	?	0.7985





Validity of Noether's ratio rule requires that the different values in each row of Table 15 are nearly the same. This is fulfilled as well as we might expect. Application of the "simplified" product rule is shown in Table 16.

Table 16.

	$\frac{\nu_1^1 \nu_2^1 \nu_3^1}{\nu_1 \nu_2 \nu_3}$ obs.	$\frac{m_H}{m_D}$	$\frac{\nu_4^1 \nu_5^1 \nu_6^1}{\nu_4 \nu_5 \nu_6}$ obs.	$\sqrt{\frac{m_H^3}{m_D^3}}$
CH <sub>3</sub> Br-CD <sub>3</sub> Br	0.517	0.500	0.412	0.354
CH <sub>3</sub> Cl-CD <sub>3</sub> Cl	0.526	0.500	0.417	0.354
CH <sub>3</sub> OH-CD <sub>3</sub> OH	0.544	0.500	0.420	0.354
CH <sub>3</sub> OD-CD <sub>3</sub> OD	0.533	0.500	?	0.354
CH <sub>3</sub> NO <sub>2</sub> -CD <sub>3</sub> NO <sub>2</sub>	0.545	0.500	0.485	0.354

The last comparison is not entirely justified. The molecules in the last three rows have symmetry properties different from those of the methyl halides and therefore, they belong to a different point group, namely C<sub>s</sub>, while the methyl halides belong to the point group C<sub>3v</sub>. The vibrations of the molecules of both point groups cannot, in a strict sense, be compared since they belong to different species. That the discrepancies are not greater may be understood when considering that the groups OH, OD and NO<sub>2</sub> may, in many vibrations, be taken as single units or "big atoms" to a good approximation. In doing so, i.e., neglecting motions within these groups, the higher symmetry C<sub>3v</sub> may be used for describing the vibrations.



## SUMMARY

A brief description of the vibrational motion of polyatomic molecules has been given, using the models of the harmonic and anharmonic oscillators. The secular equation, which gives the zero-order frequencies of the different vibrations in a molecule, was introduced. It was pointed out how the isotope effect may be helpful in the calculation of force constants and in obtaining information about the structure of molecules.

Symmetry properties of molecules and vibrations were described with special reference to point groups  $C_{2v}$  and  $D_{\infty h}$ . The notation used to indicate the different species in these groups was introduced and tables containing the characters of the symmetry types were included.

The Redlich-Teller product rule was discussed. This is a rule which relates the vibrational frequencies belonging to a certain species in a molecule with the corresponding frequencies of the isotopic molecule, in an expression which is independent of the force constants. This rule was applied in its strict form to deuterium substitutions in bent triatomic molecules of point group  $C_{2v}$  and in an approximated form to other isotopic substitutions in bent triatomic molecules and in linear triatomic molecules



of point group  $D_{\infty h}$ . The numerical results were collected in tables.

Noether's empirical relation for the calculation of frequencies of isotopic groups in some molecules was discussed. It was shown in which limited sense the rule may be justified theoretically. This was amplified by discussing a number of examples.





## BIBLIOGRAPHY

1. G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Company, Inc., New York, 1946.
2. J. H. Hibben, "The Raman Effect and its Chemical Applications," Reinhold Publishing Corporation, New York, 1939.
3. C. J. Brester, Kristallsymmetrie und Reststrahlen, Diss. Utrecht, 1923, and Z. f. Physik 24, 324 (1924).
4. E. Wigner, Göttinger Nachrichten, 1930, p. 133; E. Wigner, Gruppentheorie, Vieweg und Sohn, Braunschweig, 1931.
5. G. Placzek, Leipziger Vorträge, 1931, p. 71.
6. M. Bocher, "Introduction to Higher Algebra," The Macmillan Company, New York, 1929.
7. J. E. Rosenthal and G. H. Murphy, Rev. Mod. Phys. 8, 317 (1936).
8. A. G. Meister, F. F. Cleveland and M. J. Murray, Amer. J. Phys. 11, 239 (1943).
9. G. Placzek, Marx, Handb. d. Radiologie vol. VI, 2, p. 205 (1934).
10. R. S. Mulliken, J. Phys. Chem. 41, 159 (1937).
11. H. Sponer and E. Teller, Rev. Mod. Phys. 13, 75 (1941).
12. O. Redlich, Z. physik. Chem. B28, 371 (1935).
13. E. Teller, quoted by C. K. Ingold et al., J. Chem. Soc. (1936), p. 971.
14. E. O. Salant and J. E. Rosenthal, Phys. Rev. 42, 812 (1932).
15. D. M. Cameron, W. C. Sears and H. H. Nielsen, J. Chem. Phys. 7, 994 (1939).
16. G. B. B. M. Sutherland and D. M. Dennison, Proc. Roy. Soc.



London 148, 250 (1935).

17. C. R. Bailey and A. B. D. Cassie, Proc. Roy. Soc. London 137, 622 (1932).
18. C. F. Goodeve and C. P. Stein, Trans. Faraday Soc. 25, 738 (1929); H. C. Urey and H. Johnston, Phys. Rev. 38, 2131 (1931).
19. G. Hettner, R. Pohlman and H. J. Schumacher, Naturwiss. 23, 114 (1935).
20. G. B. B. M. Sutherland and W. G. Penney, Proc. Roy. Soc. London 156, 678 (1936).
21. A. H. Nielsen and Y. T. Yao, Phys. Rev. 71, 825 (1947).
22. M. S. Livingston and H. A. Bethe, Rev. Mod. Phys. 9, 373 (1937).
23. J. Bigeleisen and M. Goeppert Mayer, J. Chem. Phys. 15, 261 (1947).
24. H. D. Noether, J. Chem. Phys. 11, 97 (1943).
25. Ta-You Wu, "Vibrational Spectra and Structure of Polyatomic Molecules," National University of Peking, Kun-Ming, China, 1939.
26. O. Redlich and W. Stricks, Monatshefte f. Chem. 67, 328 (1936).

















